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CONTENTS

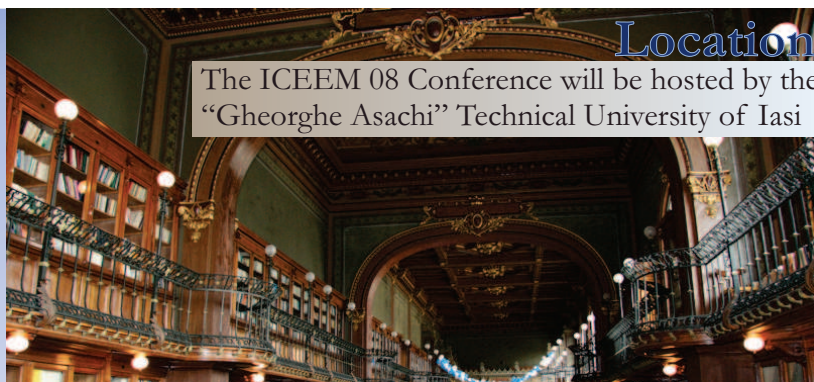
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Papers

Planned and autonomous actions: Belgrade waterfront adaptation to climate change <i>Nada Lazarevic Bajec, Marija Maruna</i>	1
Kinetic modeling of diesel oil wastewater degradation using photo-Fenton process <i>Maha A. Tony, Patrick J. Purcell, Yaqian Zhao, Aghareed M. Tayeb, M.F. El-Sherbiny</i>	11
Batch and column removal of Chromium (VI) from aqueous solution using polypyrrole <i>Ehsan Hasani, Maysam Farnam, Seyed Mostafa Hosseini Asl, Reza Katal, Seyed Omid Rastegar</i>	17
Distribution of heavy metals in the Lake Talkša (Lithuania) sapropel and possibilities of practical use <i>Justyna Kozlovska, Algirdas Dumčius, Vaida Šerevičienė, Egidijus Petraitis</i>	29
Optimization of reduction of copper using <i>Stenotrophomonas maltophilia</i> PD2 biomass and artificial neural network modeling <i>Arpita Ghosh, Papita Das (Saha), Keka Sinha</i>	37
Characterization of first flush in urban highway runoffs <i>Hamid Iqbal, Muhammad Anwar Baig</i>	45
Examination of the use of ammonium acetate as lixiviant in recovery of zinc from waste batteries and kinetic analysis <i>Nizamettin Demirkıran</i>	51
Magnitude of damage events on hydrotechnical torrent control structures <i>Ioan Clinciu, Ion-Cătălin Petrișan, Mihai-Daniel Niță</i>	57

Electromagnetic pollution of the hospital environment due to new generation mobile phones <i>Vlad Dafinescu, Valeriu David, Doru Andritoi, Eduard Lunca, Elena-Niculina Dragoi</i>	73
Elucidating characteristics of geopolymer with solar panel waste glass <i>HuiCong Hao, Kae-Long Lin, DeYing Wang, Sao-Jeng Chao, Hau-Shing Shiu, Ta-Wui Cheng, Chao-Lung Hwang</i>	79
Catholyte-conditioning enhanced electrokinetic remediation of Co and Pb polluted soil <i>Mahdi Bahemmat, Mohsen Farahbakhsh</i>	89
Performance analysis for an irreversible combined thermionic-thermoelectric generator with finite rate heat transfer <i>Zemin Ding, Lingen Chen, Yanlin Ge, Fengrui Sun</i>	97
Substrate inhibition kinetics of malathion biodegradation and the effect of molasses as cosubstrate <i>Djaber Tazdaït, Nadia Abdi, Hakim Lounici, Nabil Mameri</i>	109
Short-term responses of nitrous oxide fluxes to nitrogen and phosphorus addition in a peatland on the Tibetan Plateau <i>Yongheng Gao, Huai Chen, Martin Schumann, Yuyuan Wu, Xiaoyang Zeng</i>	121
Adsorption properties of activated carbon from wild plant prepared by chemical activation <i>Özgül Gerçel</i>	129
Causal analysis on the specified paroxysmal water pollution incidents in the Huai River Basin, China <i>Yongyong Zhang, Dunxian She, Jun Xia, Xiaoyan Zhai, Qiting Zuo</i>	139
Anaerobic bioremediation of PAH-contaminated soil: Assessment of the degradation of contaminants and biogas production under thermophilic and mesophilic conditions <i>Tahseen Sayara, Monika Čvančarová, Tomáš Cajthaml, Montserrat Sarrà, Antoni Sánchez</i>	153
Product ecodesign in companies with ISO 14001 certified environmental management system <i>Gregor Radonjič, Aleksandra Pisnik, Damjan Krajnc</i>	167
Estimating crown closure of forest stands using Landsat TM data: A case study from Turkey <i>Alkan Günlü, Emin Zeki Başkent</i>	183
Evaluation and abatement of environmental noise. A case study for district heating plant placed in a residential area of Brasov – Romania <i>Mihail-Tudor Marcu, Veneția Sandu</i>	195
Research and trends in product life cycle management in the context of sustainable development <i>Petrică Corăbieru, Anișoara Corăbieru, Dan Dragos Vasilescu</i>	205

A simulation study on the diesel engine combustion process based on the field-effect analysis method of combined combustion <i>Xiang-rong Li, Lu-ming Zhao, Zhi-jie Li, Fu-shui Liu</i>	213
Forecasting the presence of Ca^{2+} and Mg^{2+} cations in mineral waters. A model based on fuzzy logic <i>Alina Ștefanache, Eduard Mihăilescu, Cătălina Stan</i>	223
Reasons for non-participation in recycling of solid waste in Northern Malaysia: A case study <i>Abdelnaser Omran, Ana-Maria Schiopu</i>	233
Correlation analysis of CH_4 emissions from paddy soils with changes in oxidizable organic carbon <i>Jiamei Wu, Xionghui Ji, Lianjie Huo, Hua Peng, Yong Liu</i>	245
Reviewer Acknowledgements	
Reviewers_2014	251



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Foreword

After two editions abroad, in Hungary and Austria, the 8th edition of ICEEM will be organized in Iasi, Romania between 9 and 12 September 2015 by the “Gheorghe Asachi” Technical University of Iasi.

This ICEEM edition aims to bring together international researchers, academics, professionals and students activating in the fields of environmental engineering and management and to support knowledge exchange and dissemination of specific research and educational programmes.

Like before, ICEEM 08 strongly encourages contributions that focus on innovation, multidisciplinary and cross-sectorial approaches related to environmental issues and sustainability.

Furthermore, the ICEEM conference welcomes contributions of young and senior scientists, and at the same time it encourages practitioners and specialists in various environmental fields to add a more practical-oriented approach to the conference sessions.

We hope that the plenary sessions, oral and poster presentations, workshops and side-events of ICEEM 08 will enhance multidisciplinary, international cooperation and effective communication of scientists, engineers and managers.

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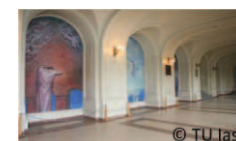
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PLANNED AND AUTONOMOUS ACTIONS: BELGRADE WATERFRONT ADAPTATION TO CLIMATE CHANGE

Nada Lazarevic Bajec, Marija Maruna*

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Abstract

There is broad consensus that adaptation to climate change is necessary and urgent. Numerous documents and guidelines are available that provide advice on how to incorporate climate hazards and risks into spatial policies on the global, European and national scale. The experiences of less developed countries have shown that, rather than simply cascading uniform procedures, methods and techniques of adaptation down from higher to lower levels of governance, a realistic approach calls for innovative procedures, tailored to specific circumstances.

The authors argue that the climate change adaptation (CCA) process in developing countries, especially post-socialist transition countries with underdeveloped institutions and procedures, differs from that seen in developed nations, which calls for taking these diverse (multiple) experiences into account when adaptation responses to particular local impacts are formulated. In that sense, adaptation is not necessarily guided by effective strategies that take into consideration overall economic, social and environmental goals, but is, rather, primarily intertwined with local spatial planning in an effort to reduce vulnerability to climate change and variability. This is mainly a reactive endeavour, as it lacks an anticipatory approach, but there are nonetheless some innovative qualities in each case that deserve to be closely inspected.

This argument is illustrated by an example from Belgrade, Serbia. The Heron Island Project on the Danube River, developed between 2006 and 2009, aimed to reduce vulnerability to flooding. In the absence of climate change adaptation policies and strategies in Serbia, the project sought to balance nature preservation with construction and CCA action. This demonstrative project can be analysed as an illustration of how climate change can be integrated into the planning system, as well as what different opportunities are available to incorporate adaptation into new and existing developments.

Key words: adaptation actions, climate change, developing countries, flood risk management, multi-level governance

Received: March, 2012; Revised final: April, 2013; Accepted: April, 2013

1. Introduction: Adapting to climate change

Scientific research summarised in the IPCC Fourth Report (IPCC, 2007) agrees on the assessment of the intensity of climate change (CC) and the threats it entails. We may therefore view the impact of climate change as a long-term natural disaster (Creig, 2010) that calls for comprehensive adjustment to regulatory and management tools.

The need to integrate CCA into all spheres of public policy-making also lends new weight to spatial planning and institutional change. Climate

change adaptation (CCA) was not adequately positioned in research and international policies at the initial stage of seeking adequate responses to CC. The emphasis on mitigation has since 2001 expanded to include adaptation (IPCC, 2001), as reflected in a range of newly-adopted documents, from the international (UN and EU) to the national, regional and local levels (Schipper, 2006).

In an effort to combine both types of policies, researchers seek an optimal mix of adaptation and mitigation. These policies are tightly interwoven, and reflect the view that more successful adaptation and

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diminished vulnerability to CC reduce the need for climate change mitigation (CCM) (Burton et al., 2002).

Moreover, there is the distinction in theory as well as in practice between autonomous or spontaneous adaptation – defined as adaptation by households, businesses and communities acting on their own in the absence of established strategies – on the one hand, and, on the other, planned adaptation, defined as adaptation that is positioned within an established strategic framework (IPCC, 2001; Klein et al., 1999; Malik et al., 2010). Autonomous adaptation is usually reactive (ex-post) while deliberate, planned adaptation is proactive (anticipatory). Reactive adaptation measures are implemented in response to current climate variability and observed impacts. Conversely, anticipatory adaptation measures are undertaken before impacts are observed, in order to reduce exposure to future risks. Given the uncertainty surrounding climate change, the implementation of anticipatory measures is challenging, as they require in-depth information and knowledge of climate change (Klein, 2002).

Climate change research in general pays little attention to local adaptation experiences, examples of adaptation to extreme climate phenomena, and historical climate variability. It is stressed that, given that the world is increasingly faced with risks of CC that are at the edges of human experience, studying lessons from the past is extremely important for understanding adaptation strategies and processes by which adaptation takes place (Adger, 2003; Adger et al., 2003).

In the absence of institutional/organisational change, lack of information, knowledge and experience of managing development in the face of new challenges, CCA actions in developing countries can for the most part be classified as autonomous and reactive. On the one hand, that practice testifies to the realistic potential for dealing with climate extremes in low- or middle-income countries, and, on the other, points to the diversity of autonomous ideas that can be incorporated into integral adaptation strategies in the future.

The fact that, in less developed environments, the need to react to climate change comes before the development of proactive policy frameworks, emphasises the necessity of exploring the potentials for diversified approaches that would recognise local realities.

The aim of this paper is to demonstrate the importance of analysing CCA actions in local communities and finding out how adaptation ideas are formed and enter the policy arena. We argue that identifying the flows of initiatives and policies in response to climate variability should be a prerequisite for thoroughly understanding which governance mechanisms are required to ensure the scaling-up of policy and successful adaptation in specific circumstances.

2. Research framework

When one refers to CCA, one usually has in mind “actions taken by governments including legislation, regulations and incentives to mandate or facilitate changes in socio-economic systems aimed at reducing vulnerability to climate change, including climate variability and extremes” (Burton et al., 2002). Some sources define adaptation as any adjustment, whether passive, reactive or anticipatory, that is proposed as a means of ameliorating the anticipated adverse consequences associated with climate change (Smit et al., 2000). This study is focused on autonomous adaptation, classified not just as individual, spontaneous (IPCC, 2001), reactive, implemented by households or businesses, but also as action towards managing risk from excessive climate change that is not part of strategic policy.

Integrated adaptation actions are viewed as top-down, from the international, taken by organisations such as the UN and the EU, to the national, and, further down, to local levels (Margulis et al., 2008). Such a hierarchical approach requires thorough organisation, well-developed institutions, articulate actors, clear mandates, etc. Coordinated, strategic, planned CCA actions, comprising policies, programmes, measures and economic assessments, are deemed to be superior. If such actions are well-suited to the system within which they are carried out, with properly developed tools for implementation, they possess the potential to deliver considerable long - term effects for reducing vulnerability to CC (Smit and Pilifosova, 2001).

On the one hand, the state is by all means the major player, as a signatory of international agreements and the only entity with the authority to enforce them (Giddens, 2009). The national government level is also expected to help build adaptive capacity, i.e. establish regulatory, institutional, governance-related and financial conditions to support adaptation actions. This requires the engagement of both national authorities and other segments of society in defining strategies and policies, building the institutional framework, providing information, enhancing knowledge, etc. Activities at the local level are considered important but have to be embedded in the national strategic and policy framework. On the other hand, Giddens points to the emergence of a new system of governance that is characterised by the struggle for authority and division of interests, the assumption of power for decision-making and the taking of measures at the regional and local levels that may not be long-term or aligned with one another, but do provide answers to the problems identified. Local actors are re-defining their roles and, instead of endeavouring to defend the present, are coming up with creative solutions for the future (Giddens, 2009). Authorities at lower levels of government thus gain an important strategic role in overcoming the impact of CC, particularly through various forms of planning.

The problems and limitations of the efficiency and effectiveness of the synergy of different climate and socio-economic change scenarios seen in the top-down approach have redirected focus towards the potentials of bottom-up adaptation actions. The vulnerability - based approach that relies on understanding and mitigating vulnerabilities, rather than on scenarios and precise projections (like the hazards-based model), requires a better understanding of the context. It is at its most suitable in circumstances where existing risks are inadequately managed or pose great uncertainties with regard to future climate impacts, and where climate and other factors are firmly intertwined, primarily in short-term planning with limited funding. Developing countries often resort to policies focused on short-term improvements through the management of existing climate-sensitive risks which at the same time attempt to cover a range of possible climate projections (Füssel, 2007).

2.1. Strategic approach

Generally, the strategic, integrated approach calls for interlinking adaptation policies with all areas of public policy. The level of governance to start with is the national level, which lays out the necessary framework for actions addressing CC challenges. It is also recommended that adaptation actions are developed as a part of various sectoral policies. Developing countries are also expected to define concrete adaptation strategies and plans, along with action programmes at the national level, and to integrate them into the work of government structures. National adaptation strategies provide skeletal support for harmonised management at lower levels of hierarchy, and the implementation of plans and projects in compliance with general policies and criteria.

Climate-change-adaptation-related actions shaped by international (UN, EU) documents involve deliberate coordinated anticipative actions taken at different decision-making levels of government. This includes legislation, regulations and initiatives aimed at reducing vulnerability and building resilience to climate change, including climate variability and extremes. In order to achieve a high degree of adaptation, the government must meet certain criteria. First of all, according to IPCC, 2001, the importance of a stable and prosperous economy is emphasised, as are delineated roles and responsibilities for the implementation of adaptation strategies. It is also argued that problems and limitations associated with CCA policy and integration of climate policy into all other public policy areas call for realistically assessing all possible courses of action and opting for an adequate one (Swart et al., 2009).

The role of the highest level of government in setting an effective policy and institutional framework, as well as in providing information, knowledge and resources for adaptation, is definitely

important, though not necessarily crucial. Governance processes cut across sectors, along horizontal and vertical lines, from the local to the global level and vice versa. The key problem in policy formulation and integration is to ensure coherency of actions and define responsibilities.

2.2. CCA and spatial planning

Spatial planning plays an important role in the implementation of climate change adaptation measures and policies; in this sense, entities are urged to broaden the scope of all plans and programmes with potential effects on risk and vulnerability (EC, 2000; EC, 2003; EC, 2007). Issues are raised of the character of planning, types of measures and cooperation with other sectors (e.g. integrating land use planning and water resource management in support of risk mitigation) as is, in particular, the need for stronger integration with civil protection measures. In that sense, climate change adaptation should become an integral part of the planning process, paralleling, for instance, the way in which environmental impact assessment is today integrated into all strategic plans and projects (Peltonen, 2006).

Climate change has largely changed the planning context and priorities. A new rationale for coordinating actions and integrating policies has been introduced (Davoudi et al., 2009). As pointed out in research, the risks associated with CC or other changes need to be assessed on a practical level (Smit and Wandel, 2006), linked with land use objectives, and further coordinated with development objectives that are consistent with adaptation (Schipper, 2007).

Complex problems such as CCA can be overcome by establishing a framework for integrated development, e.g. through “strategic planning which anticipates new tendencies, discontinuities, and surprises; it concentrates on openings and ways of taking advantage of new opportunities. Strategic plans are defined as frameworks for action” (Albrechts, 2004). In challenging development conditions, the problem is how to change traditional legally-binding land-use planning that is well-established in practice, passive, pragmatic, and that provides “physical” solutions to social or economic problems. Identifying the feasible boundaries of change within a planning regime that would provide at least some opportunities for successful CCA actions is important, as its learning potential for broader changes could be vital (Lazarevic Bajec, 2009).

3. Methods

In this exploratory paper the focus is on the Heron Island case study, which demonstrates the experience of the local community in using available instruments to develop a pilot project for the introduction of autonomous CCA actions. Multiple methods were used to establish the project design

process and investigate how adaptation actions influence strategies made at higher levels of governance. Firstly, policy documents at the national and local levels were analysed to establish the state of CCA activities in Serbia. Although there had been no official CC policies prior to 2010, a close reading of existing sector policies in the fields of environmental protection, water management, disaster protection, spatial planning etc. helped identify some links with strategic and statutory documents. Secondly, interviews with policymakers and planning professionals who played an important role in the project development were recorded and analysed. The purpose was to establish local strengths and weaknesses, and to discover what adaptation knowledge base was used in the project and how external influences shaped spatial ideas that helped integrate CCA concerns into the project.

Thirdly, international and national government policy documents, reports, and instruments were assessed in order to find out possible directions for changes to the hierarchical mode of governance towards a more collaborative one that would enable the integration of innovations into CCA policymaking in Serbia.

Because CCA is a new field of policy in Serbia, it was difficult to directly trace policy interplay from the bottom up. Analogies were therefore made with other (environmental) spatial policies with longer traditions, and, based on this approach, assumptions were arrived at of how the bottom-up policy might work.

4. Case Study: Heron Island Project

The argument of this paper is illustrated with an example from Belgrade, Serbia. The Heron Island Project on the Danube River, developed between 2006 and 2009, aimed at reducing vulnerability to flooding and sustaining waterside ecosystems that have essential environmental functions. In the absence of climate change adaptation policies and strategies in Serbia (Lazarevic Bajec, 2009), the project sought to balance nature preservation and construction through CCA action. This demonstrative project can be analysed as an illustration of how climate change can be integrated into the planning system, as well as of which different opportunities for systemic change are offered by local initiatives.

Although many autonomous activities geared towards CCA can be discerned in Serbia, they are often not recognised as such, but are rather connected with defence against natural and technological hazards, sustainable development, and the like. Climate change adaptation did not feature at the policy level in Serbia until its first mention in the The Law on Spatial Plan of the Republic of Serbia from 2010 to 2020 (SPRS, 2010) and Serbia's first Initial National Communication under the United Nations Framework Convention on Climate Change (Bozanic and Gasperic, 2010). These documents give clear support to a strategic hierarchical approach as an

essential prerequisite for the implementation of concrete measures in managing CCA actions.

The Heron Island Project entails the formation of a new island on the foreland of the left bank of the Danube (separating it from the mainland and protecting its forests, swamps, canals and potential beaches) that would stretch across 582 hectares and be intended for a multipurpose tourist, sports and recreation centre. The project was developed in cooperation with the Town Planning Institute of Belgrade and the University of Florence. Underpinned by planning principles that merge land use with social and ecological planning, the project prioritises policies designed to avoid adverse impacts of natural hazards by providing flood spillover areas in case of elevated water levels.

The project offered an opportunity for a detailed examination and implementation of goals and objectives defined by the Belgrade Master Plan 2021 adopted in 2003 (Fig.1). Thus, in the absence of an integrated water resource management strategy, it anticipates the shift from traditional "flood defence" to innovative flood management, characterised by designating land for mixed use, including tourism and recreation; strengthening natural resources through the formation of a protective green belt around the city; and reducing the risk of climate-related disasters while safeguarding the authentic vegetation of foreland, pond and swamp ecosystems in order to preserve the Danube River waterfront as it looks today and contribute to landscape preservation and development (Fig. 2).

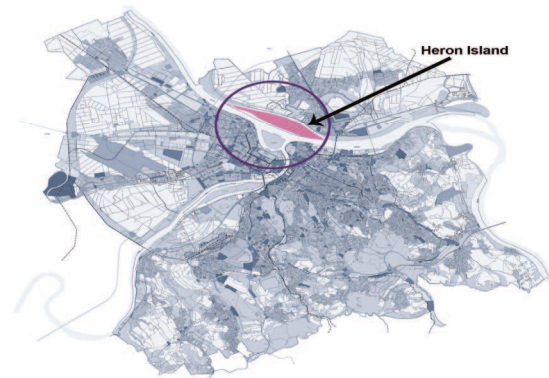


Fig. 1. The Belgrade Master Plan 2012 recognised the confluence of three river branches, the existing islands and the new Heron Island as the *genius loci* of the city and the main focus of care and protection, as well as the site driving genuine future development (TPBI, 2003)

The Heron Island Project is based on projections that indicate climate change may cause more intense flooding and drought episodes (Fig. 3), greater in both their scope and duration. The project is a response made by local professionals to the idea of Belgrade's expansion onto the left bank of the Danube formulated in the Belgrade Master Plan 2021 (TPBI, 2003).

It is also an answer to the official position of the National Water Management Agency that there will be no government intervention to construct or

raise river dykes for preventing flooding along that part of the river. The basis of the project is the acceptance of an ecological approach that sustains the capacity of ecosystems to respond with resilience to external changes, which fits in with adopted national policies and strategies on sustainability.

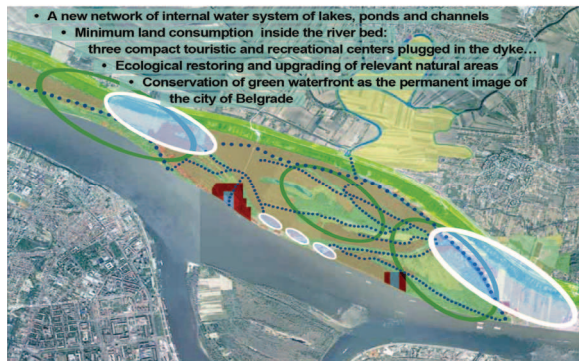


Fig. 2. Heron Island Project (Source: Lazarevic Bajec, adapted from Town Planning Institute, 2009)

4.1. Adaptation to flooding

The shift from the standard mode of thinking in the Heron Island Project was provoked by a study conducted by Varga and Babic-Mladenovic (2001).

This study, unusual in local terms, presented international water management experiences and recommended the abandonment of the “flood fighting principle”, which relies on large-scale and investment-intensive construction (dams, accumulations, dykes, watercourse management, flood relief channels etc.), in favour of “living with floods”. It is a new, integral concept of flood protection that fits in with the concept of sustainable development, striving to balance the “human” component (the safeguarding of human lives and protection of property) with the “environmental” one (preservation or recovery of natural functions and resources of a flooded area) (Varga and Babic-Mladenovic, 2001).

It should be noted that this new approach introduced in the Heron Island Project was not in line with official flood protection policies adopted by Srbijavode, the National Public Water Management Enterprise, which favours building massive facilities and systems. Formulating the official national formal flood control policy in Serbia is the task of the water management sector, and is embodied in the General Flood Defence Plan and the Annual Plan for Flood Defence, which are in turn supported by a programme of investment into infrastructure. It is important to underline that plans are prepared only for watercourses with existing flood protection structures. Other locations are left to be dealt with local communities (ICPDR, 2009).

4.2. Exogenous knowledge

The authors of the Heron Island Project place special emphasis on the experience of the

Netherlands, with its new “Room for the River” policy, a tailor-made, flexible approach to water management. This national programme, launched in 2006 and due to finish in 2015, relies on a climate change forecast to 2050.

“The menu of existing adaptive measures, compiled through learning from the past, may however not be sufficient to enable policymakers to select projects to maximize net benefits with climate change, as future climate patterns may be very different from current patterns. Thus it is important to complement understanding of current adaptation measures with identification of additional measures that may be needed to deal with projected climate variability.” (Margulis et al., 2008).

Key adaptation measures under the Heron Island Project go along the lines of linking water and land use, incorporating alternative flood risk management into innovative mixed land use practices, master landscaping and improving overall environmental conditions, etc.

The project envisages the construction of island settlements in the form of floating structures – floating villages – located on water canals that will cut through the island and be accessible from the river (TPBI, 2003).

The authors’ vision of the project is that of a “model of development harmonic with natural environment, an approach that at the same time introduces a dialogue with the pure Belgrade tradition of intimacy with the great river” (TPBI, 2009).

What is poetically dubbed “intimacy” is actually a set of autonomous actions of adaptation to climate change and variability, floods and storms, non-planned and spontaneous, which have a decades-long history in the Sava and Danube riparian area (along a 153 km stretch of riverbank in Belgrade). A variety of shoreline activities have made innovative use of the riverbanks, discovering autonomous adaptation modes. Houses, rafts, boats, and marinas that have emerged outside of the system of official policies and control have markedly changed the waterfront landscape (Fig. 4).

4.3. Endogenous knowledge

The authors of the project display an awareness of the importance of detailed design guidelines. Learning from experience, they propose light constructions, floating houses, linked to the tradition of spontaneous construction on Belgrade’s rivers (autonomous adaptation), leaving the landscape uninterrupted, interacting directly with the alternately rising and falling water level of the Danube. However, concrete technological solutions are modelled on international practice (Canada, the Netherlands, UK, and USA) (Fig. 5).

Interestingly, the proposal to use floating structures, the autonomous form of adaptation on Belgrade’s rivers, the Danube and the Sava, whose levels commonly dramatically oscillate and which

are prone to flooding, came from Italian partners on the project. The local professional community needed international validation to integrate autonomous forms into planning proposals. Planners from the Town Planning Institute of Belgrade commended the approach applied by Giovanni Ruffini, an architect from the University of Florence, who suggested floating structures as a prevailing modality of “construction” for continuing the tradition of using riversides in Belgrade (TPBI, 2009).

The approach envisages the siting of floating villages on water in the new internal lakes, and along stretches of water and canals (TPBI, 2009). In addition to embracing autonomous adaptation forms as a functional solution to persistent threats of flooding, the project promotes floating structures and pile dwellings as an integral part of Belgrade’s identity and the city’s relationship with its rivers (Fig. 6). The proposed alternative to riverside construction on solid soil, which would require erecting costly levees, are floating villages, following years-long practice of adaptation to climate variability on river banks that has given rise to a specific landscape. In this way, rather than being denied, unplanned and autonomous experiences are embraced, tested and embedded into local spatial projects and plans.

It seems only natural that, given the limited experience and knowledge in the new policy field, local actors should turn towards established (international) authorities. The outcomes of the communication and learning process are expected to be greater self-confidence, lessons learned on how to interpret successful spontaneous adaptation examples, and altogether advanced adaptive capacity.

5. Discussion: bridging the gap

Unlike in developed economies, a CCA policy framework is only now starting to emerge in transition (post-socialist) and developing countries such as Serbia. Local adaptation policies are not adequately supported at higher levels of governance. At the national level, CCA is mostly considered in the context of recommendations by international organisations, fraught with persistent frustrations of decision-makers, researchers, planners and other stakeholders involved in CC response activities who are unable to respond to requirements from the international (EU) level and adequately position and coordinate their efforts, or, rather, to translate the mitigation of vulnerability into on-going CC adaptation actions.



Fig. 3. Emergency repairs with sandbags and flooded restaurant on the Zemun waterfront in Belgrade at high water levels in 2006 (Lazarevic Bajec, 2009)



Fig. 4. Autonomous forms of adaptation: floating restaurants and homes on the Danube and Sava rivers in Belgrade (Lazarevic Bajec, 2009)



Fig. 5. Utrecht (Holland) floating houses (deliberate CCA actions) (Lazarevic Bajec, 2009)



Fig. 6. Autonomous adaptation to flooding on the Sava and Danube Rivers (Lazarevic Bajec, 2009)

There is a gap between the procedures proposed by researchers and international organizations and the ill-fitting system of government (Slunge et al., 2008). Against the backdrop of poorly developed national framework, climate changes, variability and hazards all provoke bottom-up actions.

Integrating autonomous adaptation experiences into development policies is much more important for developing than for developed countries because of their greater vulnerability, limited resources, low level of technology, institutional inefficiencies etc. The planning model in developing countries, especially post-socialist transition countries with under-fledged institutions and procedures, differs from that applied in developed countries, urging the adopted planning model to make room for the identification of successful instances of autonomous adaptation, interaction between autonomous and planned actions, and top-down and bottom-up initiatives. This is the reason why it is argued that, in less-developed countries, adaptation can be effective only when linked to local development issues. It should be noted that in developing countries the general problem is the lack of capacity to produce good strategies, both development-related and adaptation ones, and the challenge is to manage the necessary actions in that specific situation.

Multi-level governance is the key for successful integrated adaptation policies. However, in many countries with strong centralised hierarchical traditions, establishing a coordinated governance system is no easy task. The fact that coordination, both horizontal and vertical, is considered a crucial precondition for the successful implementation of CCA should not discourage adaptation from taking place at the local level. The concept of strengthening local-level governance in Serbia should be supported, and space for independent local CCA projects secured, regardless of whether they operate within a national strategic framework or depend on international assistance.

Local authorities strive for more influence on the adoption of national policies, on the coordination of policies relevant for local development, and on the institutionalisation of local representation in national government (Damjanovic et al., 2011). However, scaling bottom-up strategies up into national policies is an issue of governance reorganisation connected

with power relationships. Even after a decade of democratic development in Serbia, local authorities have yet to enjoy success as agenda setters. For example, local governments in the Danube River basin have to date achieved operational independence in flood risk management in only a few cases (Belgrade, Novi Sad, Smederevo). They have reconciled conflicting policies through urban planning by introducing innovative flood protection ideas, although they have brought about no changes in formal water management strategy.

The project has encouraged local communities on the right bank of the Danube to protest against official policy and put pressure on policy changes and the extensive reconstruction of levees that are changing the landscape of the historic city. They expected CCA adaptation integrated into local urban planning criteria to produce better flood protection solutions. Although the Serbian Water Management Agency has refused to change its policy, in this case there have been some changes in the approach to flood defence plans. Recent strategic documents have modified the water management approach and defined targets and measures to be taken for regulating land use and spatial planning, increasing retention and detention capacities, as well as building capacity and raising preparedness (ICPDR, 2009).

As in other developing countries, a two-tier CCA approach can be expected in Serbia (Lemos et al., 2007). On the first tier, efforts would be focused on the establishment of effective climate disaster management, in response to direct hazards related to CC and climate variability. Adaptation policies are predominately intertwined with local spatial plans, which are usually the best-developed form of such planning. The second tier would include the implementation of reform policies addressing structural problems related to inequalities and human vulnerability, working on new forms of governance at local and national levels, and building adaptive capacity among government bodies, businesses, scientists, and individuals. Thus, adaptation efforts can act as a trigger for transformation and change in governance structures (Fig. 7). Although extensive research and documents produced by international organisations do put forward the most efficient and effective procedures aimed to respond to CC challenges, there is clearly no uniform solution. As put concisely by Creig: “The problem is, in this brave new world of climate change adaptation, there will be

no panaceas – ‘one size fits all’ solutions to environmental problems – particularly in the realm of natural resource management” (Creig, 2010).

The case of the Heron Island Project can serve as an appropriate illustration of a practical response to CC and variability hazards against the backdrop of an underdeveloped policy and regulatory framework. Given the lack of coherence between higher and lower levels of government, the Project is in line with the advice to formulate “easy adaptation measures” as a way to raise public awareness and encourage development of plans and regulations in different sectors, ultimately leading to adaptation to variable climate conditions (Nagy et al., 2008). This practice may be risky because there is no strategic agreement and the realisation of projects is questionable.

However, at the same time, it allows for experiments and innovations that may hopefully lead to system adaptation. The importance of the Heron Island Project lies not only in its quality and proposed adaptive actions, but also in the manner, process and method of planned CCA actions, which,

in the absence of national strategy, use the results of international policies and mix them with traditional informal experiences. However, given the poorly-developed policy and regulatory framework in Serbia, the path of shaping ideas and concepts was not straightforward. Local experiences in tackling flooding were validated by comparison with foreign examples founded on research and assessment-supported adaptation strategies. The cooperation with Italian experts, who provided the relevant information, knowledge, and experience, boosted the self-confidence of local experts and enabled them to recognise good solutions in their own environment and use them creatively.

The project also takes into account the fact that CC creates a dynamic environment, prompting the search for innovative solutions, different from the common top-down planning approach that reduces adaptation measures to large-scale infrastructure-based interventions associated with physical protection, such as the massive concrete levee being built to replace the old stone one in Zemun (Fig. 8).

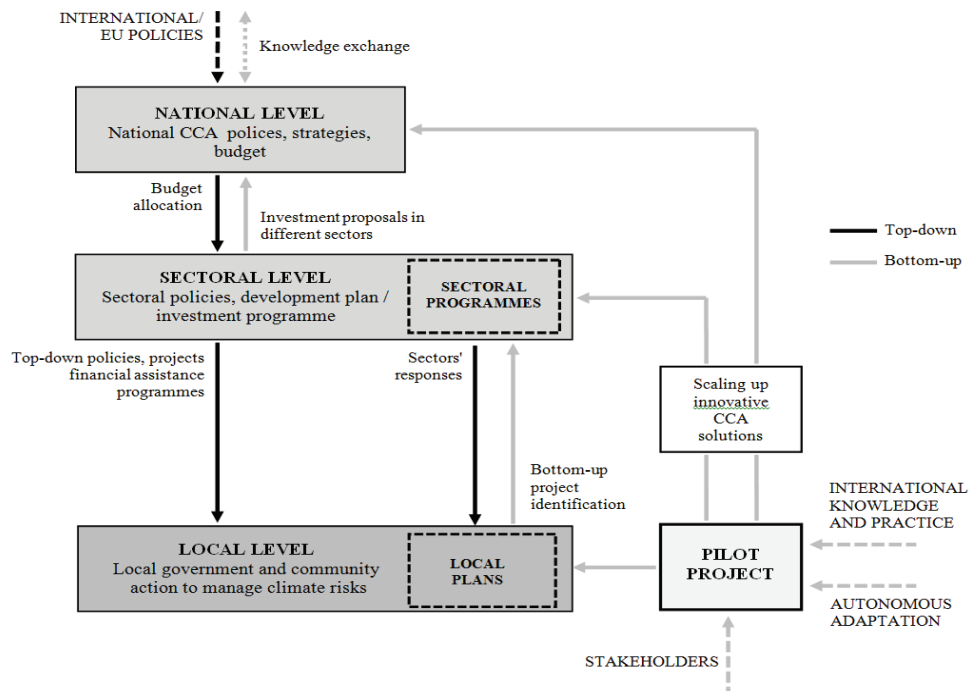


Fig. 7. Delivery of adaptation through the planning system in Serbia. Role of local projects and external influences (modified diagram from OECD, 2009)



Fig. 8. Flood protection structure on the right bank of the Danube: Old and new levees (Lazarevic Bajec, 2009)

6. Conclusions

The paper analyses some features of procedures and methods for formulating CCA actions that are altering the urban landscape of Belgrade, Serbia. A detailed description of the Heron Island case was presented so as to give insights into the process and define the place of local projects in the system of CCA decision-making in Serbia. The idea is to understand the potentials of a bottom-up local CCA project and to analyse the influence such projects might have in developing a multi-level system of governance.

The Heron Island Project, presented in the paper, is an authentic product that emerged from familiarity with local circumstances, different spatial development requirements, proposals modelled on local traditions, and knowledge generated from experience. Although uncertainty may make it difficult to fine-tune adaptation, there are grounds to assume that the CCA approach applied in the project will ensure sustainable solutions and coordination with the Directives from EU level, considered key tools for cross-border cooperation and the adaptation of the water sector to climate change.

Spatial planning, which is in most countries institutionalised and based on the principles of environmental sustainability, can play a significant role in CCA. In addition, given the limited knowledge of local planners in this field, emphasis should be placed on the integration of planning and science, a trans-disciplinary approach that would facilitate the search for adequate responses to specific problems induced by CC. Spatial planning in Serbia can be expected to adopt a more strategic approach and develop flexible and adaptive planning instruments in the future.

This paper presents a CCA case study in seeking to assess the relevance of local autonomous actions for the transformation of urban planning in Serbia into a model that relates to the country's changing institutional organisation, social and economic relations, and governance structure. It is argued that the planning model in developing countries should make room for the identification of successful autonomous adaptation, interaction between autonomous and planned actions, and integration of bottom-up initiatives into policy making.

The Heron Island Project, though not employing the current rhetoric of CCA adaptation and mitigation, is actually aligned with all contemporary requirements in this area. One should not over-romanticise local initiatives and creative capacities. The paper emphasises a bottom-up approach to integration that effectively combines local capacities with those from external experts, and so contributes to the building of the necessary national CCA policy framework, an important step towards a more strategic approach in planning.

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KINETIC MODELING OF DIESEL OIL WASTEWATER DEGRADATION USING PHOTO-FENTON PROCESS

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Abstract

The objective of this study is to develop a mathematical model which would confidently predict the rate of substrate degradation of an oil-water emulsion in a laboratory-scale completely-mixed continuous flow reactor using the photo-Fenton treatment process. Two models are developed from first principles and the predicted substrate removal rates for both models are compared with experimental data. The principal conclusions of the study are that both models produce good correlations with the experimental data at moderate to long hydraulic retention times, but, at short hydraulic retention times, there is some divergence between the predicted and measured data. This disparity may be attributable to a greater degree of short-circuiting through the reactor at short hydraulic retention times.

Key words: diesel oil-wastewater emulsion, mathematical modeling, photo-Fenton, reaction kinetics

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1. Introduction

Oil-contaminated wastewater can have a detrimental effect on biological wastewater treatment processes. Such wastewater streams can arise from hydrocarbon processing at petroleum refineries or by accidental spillage at petroleum filling stations (Galvao et al., 2006; Tiburtius et al., 2005). Several conventional techniques such as evaporation, phase separation, filtration, dissolved air flotation, de-emulsification, coagulation and flocculation (Li et al., 2006; Portela et al., 2003) are used to treat these wastewater streams.

However, these processes may not be wholly effective since they transform the pollutants from one phase to another without complete stabilization and residual concentrations may still exist in the effluent (Andreozzi et al., 2000).

Advanced oxidation processes (AOPs) are potentially useful for treating hydrocarbon-contaminated wastewater because they generate hydroxyl radicals ($\text{HO}^\bullet$), which are powerful non-specific oxidants (Moraes et al., 2004; Zhu et al., 2013). Among these AOPs, photo-Fenton's reagent, which consists of H_2O_2 and Fe^{2+} in the presence of UV light, is added directly to the wastewater (Bauer and Fallmann, 1997; Gernjak et al., 2004; Abdullah et al., 2014). In addition to the oxidation that is carried out by the hydroxyl radicals generated by catalytic decomposition of hydrogen peroxide, the Fe^{3+} ions generated during the oxidation stage promote further treatment of other pollutants by coagulation and sedimentation. Fenton's reagent is most popular for the oxidation of wastewater containing hydrocarbons (Andreozzi et al., 2000; Coelho et al., 2006; Moraes et al., 2004; Rivas et al., 2001; Tiburtius et al., 2005).

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Additionally, Andreozzi et al. (2000) applied Fenton's reagent for the treatment of mineral oil wastewater; Rivas et al. (2001) recommended the Fenton's reagent method for the treatment of olive oil mill wastewater; Moraes et al. (2004) examined the application of the reagent for the treatment of saline wastewater contaminated with hydrocarbons.

In a previous study conducted by the authors (Tony et al., 2009), the performance of the photo-Fenton process for the degradation of a diesel oil-water emulsion was investigated. Both batch and continuous-flow studies were undertaken. The objective of this paper is to develop mathematical models of these processes and to compare the numerical predictions with the experimental data previously published (Tony et al., 2009). The models developed, coupled with the determination of the kinetic parameters in laboratory-scale batch tests, enable the performance of full-scale continuous flow processes to be predicted.

2. Kinetic models

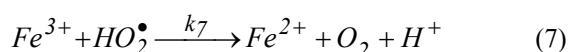
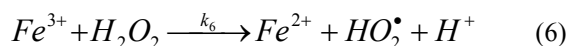
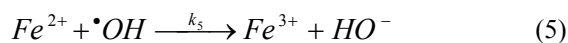
Kinetic models of the photo-Fenton's process fall into two broad categories:

(a) 'Stoichiometric' models (Chen and Pingatello, 1997; De et al., 2006; Heredia et al., 2001; Liu et al., 2007;

(b) 'Black-box' models (Chan and Chu, 2003; Dooge et al., 1984).

2.1. 'Stoichiometric' models

The 'stoichiometric' model of the photo-Fenton conversion of substrate (S) to stable end-products is given considered) is given by Eqs. (1-7) below (De et al., 2006):



Eqs. (1, 3-5) describe the generation/consumption of $\bullet OH$ radicals. The net generation may be expressed as given by Eq. (8):

$$\frac{dC_{OH}}{dt} = k_1 C_{H_2O_2} C_{Fe^{2+}} - k_3 C_{OH} C_S - k_4 C_{OH} C_{H_2O_2} - k_5 C_{OH} C_{Fe^{2+}} \quad (8)$$

Assuming the concentration of $\bullet OH$ radicals to remain stationary, that is $dC_{OH}/dt = 0$, Eq. 8 yields in Eq. (9).

$$C_{OH} = \frac{k_1 C_{H_2O_2} C_{Fe^{2+}}}{k_3 C_S + k_4 C_{H_2O_2} + k_5 C_{Fe^{2+}}} \quad (9)$$

Eqs. (2, 3) describe the degradation of substrate S, while Eqs. (6, 7) describe the Fe-redox cycle. Thus, the overall rate of degradation of substrate in solution $\left(\frac{dC_S}{dt}\right)$ can be written in the form of Eq. (10).

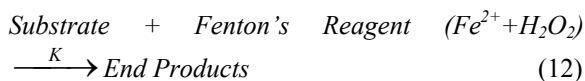
$$-\frac{dC_S}{dt} = k_2 C_S C_{H_2O_2} + k_3 C_S C_{OH} \quad (10)$$

By substituting the expression for $\bullet OH$ radicals from Eq. (9) into Eq. (10), we obtain Eq. (11).

$$-\frac{dC_S}{dt} = k_2 C_S C_{H_2O_2} + k_3 C_S \frac{k_1 C_{H_2O_2} C_{Fe^{2+}}}{k_3 C_S + k_4 C_{H_2O_2} + k_5 C_{Fe^{2+}}} \quad (11)$$

2.2. 'Black-box' models

An alternative approach to modeling the conversion of reactants to end-products is the use of so-called 'black-box' models which link 'input' and 'output' without considering any intermediate stages, as presented in Eq. (12):



A number of researchers (Lin et al., 1999; Celin et al., 2003; Coelho et al., 2006) have attempted to apply a simple first-order rate law to describe the photo-Fenton degradation of organic compounds in wastewater (Eq. 13):

$$C_R = C_o (1 - e^{-K_1 t}) \quad (13)$$

where C_o = initial substrate concentration; C_R = substrate concentration removed at time t; K_1 = decay constant.

Eq. (13) implies that the concentration (C) of the substrate remaining at any time t asymptotically approaches zero in the limit. However, some researchers have found that, in some cases, a residual concentration remains in the wastewater. It's the case of Coelho et al. (2006), who investigated the degradation of sour refinery wastewater, and found that the rate law is more appropriately described by a modified version of Eq. (13) in the form of Eq. (14).

$$C_R = C_F \left(1 - e^{-K_2 t} \right) \quad (14)$$

where: C_F = final concentration of substrate removed; K_2 = decay constant.

Other researchers, such as Chan and Chu (2003), have modeled the Fenton treatment process of atrazine and 2,4 dichlorophenol using a 'shape function', as given by Eq. (15).

$$C_R = C_F \left(\frac{t}{K_3 + t} \right) \quad (15)$$

where K_3 is the time at which the concentration of substrate removed is half its final value.

In subsequent sections, the applicability of Eq. 14 (previously applied to treatment of a refinery wastewater) and 15 (previously applied to Fenton treatment) to modeling the photo-degradation of an oil wastewater in a laboratory-scale batch experiment is examined.

3. Experimental measurements

3.1. Synthetic wastewater

Commercial diesel oil and chemical emulsifier, sodium dodecyl sulphate ($C_{12}H_{25}Na_4S$), were used to prepare the synthetic model oil-water emulsion, as described in our previous work (Tony et al., 2009). Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) and Hydrogen peroxide (H_2O_2 30% wt.) from Sigma-Aldrich were used as the source of the Fenton's reagent. The UV light was provided by a high intensity 254 nm UV grid lamp, manufactured by UVP Inc. (254 nm UV, 1250 microWatts/cm², model R-52 Grid Lamp).

The wastewater substrate concentration, with an initial COD of 404 mg-COD/L was quantified by its Chemical Oxygen Demand (COD) using a HACH analyser (model HACH DR-2400). The natural pH of the oil-water emulsion was 8.5.

3.2. Batch experiments

The first set of experiments was conducted in a batch reactor at the optimum reagent concentrations ($[Fe^{2+}]_0 = 40$ mg/L and $[H_2O_2]_0 = 400$ mg/L) and natural pH of wastewater (found to be optimum pH), which were determined in our previous work (Tony et al., 2009), as illustrated in

Fig. 1. In our previous work, it was shown that the photo-Fenton treatment of oil wastewater achieved approximately an additional 8% COD removal, when compared with the COD removal performance from the wastewater using Fenton's reagent alone. The removal of the COD concentration, plotted as a dimensionless ratio (C_R/C_0) as a function of time for the batch experiments is shown in Fig. 2.

Mathematical models, as given by Eqs. (14) and (15) above respectively were applied to the experimental data, as illustrated in Fig. 1.

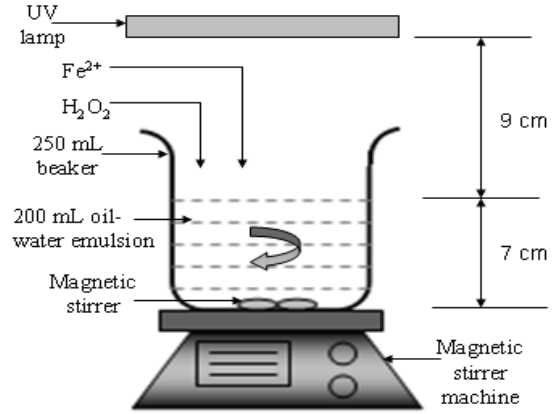


Fig. 1. Schematic of batch experimental setup (Tony et al., 2009)

To determine the experimental constants K_2 and K_3 for each model, the experimental data was plotted in a linearized format in Fig. 3 yielding values of $K_2 = 0.06$ and $K_3 = 2.88$. Examination of Fig. 2 shows that the rate of substrate conversion to stable end products can be broadly classified into two phases:

- an initial rapid conversion phase, when the rate of reaction is primarily a function of the substrate concentration;
- a final slow conversion phase, when the low substrate concentration limits the reaction rates.

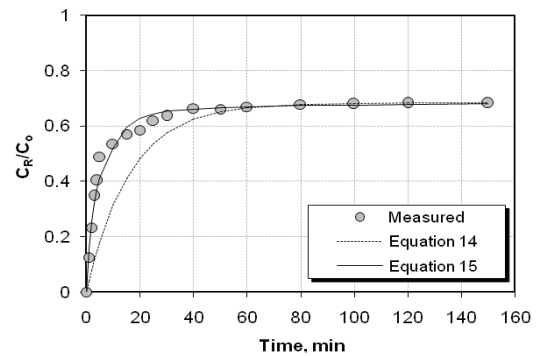


Fig. 2. Dimensionless removal ratios (C_R/C_0) in the case of the batch experiments for the photo-Fenton treatment of diesel oil wastewater

3.3. Continuous-flow experiments

In order to examine the feasibility of treating an oil-water emulsion on a large scale, a continuous-flow laboratory-scale reactor was developed, as

illustrated in Fig. 4. As shown in Fig. 4, the reactor consisted of a beaker which contained 4L of the stock solution (oil-water emulsion + Fenton's reagents). The stock solution was pumped at the following volumetric flow rates (mL/minute): 0.25, 1.25, 3.125, 6.25, 10, 16.67.

For each flow investigated, the solution was pumped at a steady rate to a 250 mL beaker which was initially filled with 150 mL of the stock solution, stirred with a magnetic stirrer and placed under UV radiation. The UV lamp was placed at a distance of 9 cm above the emulsion free-surface in the 250 mL beaker (the same as in the batch experiments). The materials and instruments used were as described in sections 3.1 and 3.2 above.

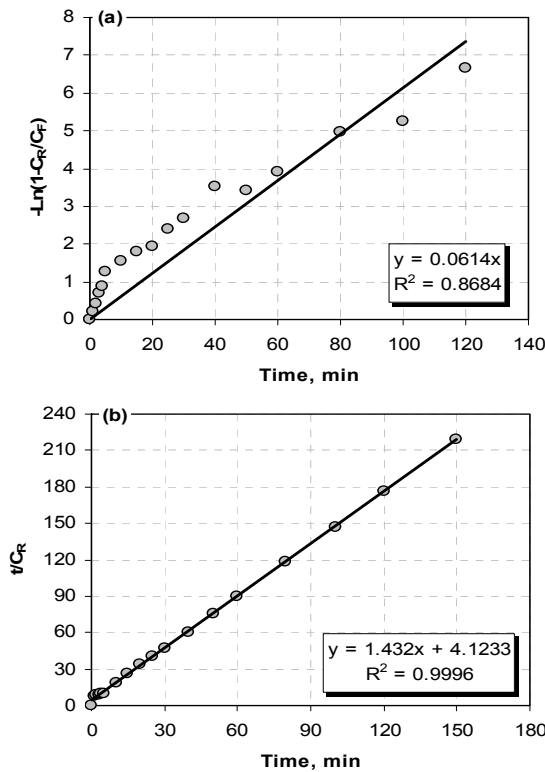


Fig. 3. Experimental data plotted in a linearized format: (a) Eq. (14), (b) Eq. (15)

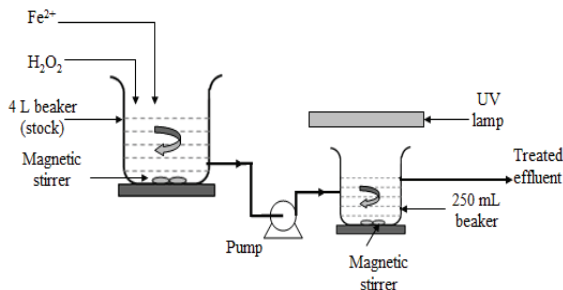


Fig. 4. Schematic diagram of the continuous photo-Fenton experimental set-up

In this series of experiments, the principal parameter investigated was the effect of the hydraulic retention time (T) in the 250 mL beaker on the

degree of mineralization of the waste, as given by Eq. (16):

$$T = \frac{V}{Q} \quad (16)$$

where: V = volume of emulsion (L); Q = volumetric flow rate (L/min).

Fig. 5 illustrates the rate of substrate removal for the continuous process operating at various hydraulic retention times.

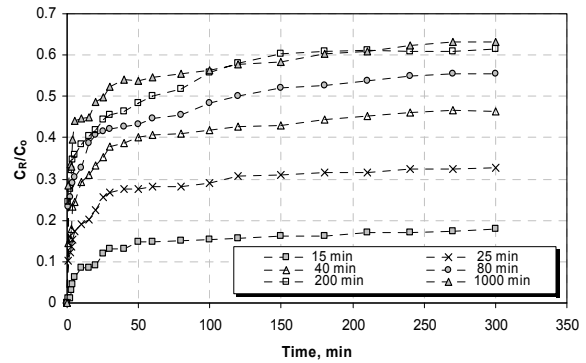


Fig. 5. Dimensionless substrate removal (C_R/C_0) rates in the case of the continuous photo-Fenton process for various hydraulic retention times

Examination of Fig. 5 shows that, following the start of each experiment, there was a transient phase during which the COD removal rates increased, followed by a phase during which the effluent removal rates remained relatively steady. As might reasonably be expected, longer retention times resulted in a greater degree of stabilization of the effluent and vice versa. These results accord with the findings of Coelho et al. (2006), who investigated the photo-Fenton treatment of a petroleum refinery wastewater.

4. Model development

4.1. Model 1

A model of the continuous flow process, assuming a completely mixed reactor, may be developed by conducting a mass balance around the reactor. The mass balance equation, assuming a steady state exists, can be written in the form of Eq. (17).

$$QC_o + V \frac{dC}{dt} = QC \quad (17)$$

Dividing Eq. (17) by Q and combining with Eq. (16) it results Eqs. (18, 18a).

$$C = C_o + T \frac{dC}{dt} \quad (18)$$

$$C = C_o - T \frac{dC_R}{dt} \quad (18a)$$

since $C + C_R = C_o$.

Differentiating Eq. (14) gives Eq. (19).

$$\frac{dC_R}{dt} = K_2 C_F e^{-K_2 t} \quad (19)$$

Combining Eq. (18a) and (19), Eq. (20) will result.

$$C = C_o - TK_2 C_F e^{-K_2 t} \quad (20)$$

$C_R = C_o - C$ implies that Eq. (20) can be re-written in the form of Eq. (21).

$$C_R = TK_2 C_F e^{-K_2 t} \quad (21)$$

By combining with Eq. (14), it results Eq. (22).

$$C_F e^{-K_2 t} = C_F - C_R \quad (22)$$

Combining Eq. (21) and Eq. (22) yields Eq. (23).

$$C_R = \frac{K_2 C_F T}{1 + K_2 T} \quad (23)$$

4.2. Model 2

A second model of the continuous flow process (Eq. 24) may be developed by differentiating Eq. (15).

$$\frac{dC_R}{dt} = \frac{K_3 C_F}{(K_3 + t)^2} \quad (24)$$

Combining Eqs. (18a) and (24) it resulted Eq. (25).

$$C = C_o - TC_F \left[\frac{K_3}{(K_3 + t)^2} \right] \quad (25)$$

Eq. (25) combined with Eq. (15) results in Eq. (26).

$$t = \frac{K_3 C_R}{C_F - C_R} \quad (26)$$

Substituting Eq. (26) into Eq. (25), the following quadratic expression, which may be solved in the normal manner for C_R (Eq. 27).

$$C_R^2 - C_R C_F \left[2 + \frac{K_3}{T} \right] + C_F^2 = 0 \quad (27)$$

4.3. Comparison of experimental results and model predictions

Eqs. (23) and (27) above were used to predict the substrate removal ratios (C_R/C_o) for various hydraulic retention times in the continuous flow reactor. A comparison of the experimental and predicted values is shown in Fig. 6. Examination of Fig. 6 shows good agreement between the model and experimental values at moderate to long retention times, whereas, at short retention times, the model over-predicts the substrate removal rates. These findings are in agreement with those of Coelho et al. (2006), who investigated the photo-Fenton treatment of a petroleum wastewater.

The disparity between the model and experimental values at short retention times may be attributable to short-circuiting of the flow through the reactor resulting in higher actual effluent COD values than predicted by the model. It is interesting to note that, although Eq. (14) exhibited a poorer fit ($R^2 = 0.8684$) than Eq. (15) ($R^2 = 0.9996$) with the experimental data in the case of the batch test, the application of model 1, developed from Eq. (14), to the continuous flow reactor resulted in better model predictions ($R^2 = 0.9694$) than model 2, developed from Eq. (15), ($R^2 = 0.9279$).

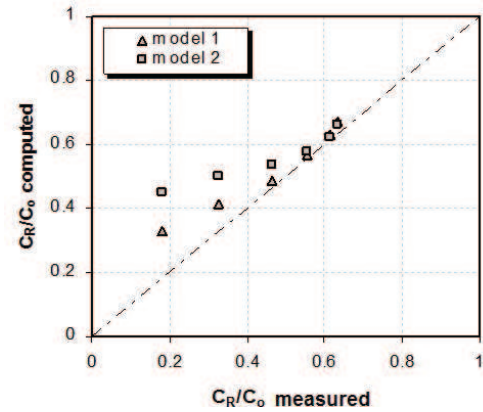


Fig. 6. Experimental and predicted dimensionless removal ratios (C_R/C_o) for the continuous-flow experiments at various hydraulic retention times

5. Conclusions

Two mathematical models of the substrate removal using the photo-Fenton method in the cases of a synthetic oil-water emulsion in a batch reactor and in a completely-mixed continuous-flow reactor have been presented.

The models of the batch processes enable the determination of the kinetic parameters for use in the models of the continuous process. The model developed enables the performance of full-scale continuous flow processes to be predicted and also enables a sensitivity analysis to be undertaken. Both models yielded good correlations ($R^2_{model\ 1} = 0.9694$, $R^2_{model\ 2} = 0.9279$) with the experimental data at moderate to long retention times, but, at short

retention times, a greater disparity between the model and experimental values resulted.

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BATCH AND COLUMN REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING POLYPYRROLE

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Abstract

The present study deals with the removal of Cr (VI) from aqueous solution by polypyrrole (PPy). Response surface methodology (RSM) was applied for the design and analysis of experiments in the optimization of pH, temperature, initial concentration, contact time and adsorbent dose during the removal of the Cr (VI). The optimum adsorbent dose, temperature, initial concentration of Cr (VI), pH and contact time were found to be 0.8 g, 46.5 °C, 187.5 mg/L, 5.3 and 15.4 min respectively. Under optimal values of process parameters, high removal efficiency (>90%) was obtained for Cr (VI). Analysis of variance (ANOVA) of central composite design showed a high coefficient of determination value ($R^2 = 0.96$) and satisfactory prediction second-order regression model was derived. Maximum chromium removal efficiency was predicted and experimentally validated. The Langmuir, Freundlich and Dubinin–Radushkevich isotherms are subjected to sorption data to estimate sorption capacity. The results gained from this study were well described by the theoretical Freundlich. Three equations, i.e. Morris–Weber, Lagergren and pseudo - second order have been tested to track the kinetics of adsorption process. The results gained from this study were well described by the theoretical pseudo - second order. The removal of Cr (VI) by PPy was also investigated in a fixed bed column. Experiments were conducted to study the effect of important parameters such as bed depth (5–20 cm), flow rate (5–15 ml min⁻¹) and initial concentration (50–300 mg/L). Also the PPy was used for the Cr (VI) removal from industrial wastewater and showed a high potential for the wastewater treatment.

Key words: batch, column, Cr (VI), polypyrrole, response surface methodology

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1. Introduction

Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below these limits even have potential for long-term contamination, because heavy metals are known to be accumulative within biological systems. One of the heavy metals that have been a major focus in water and wastewater treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties (Amin et al., 2010; Diaconu et al., 2009; Nameni et al., 2008). Rapid industrialization over the years led to an

increase and accumulation of hexavalent chromium in environment. Chromium is considered as priority pollutants because of their high toxicity at low concentrations (Mahvi, 2008; Nwuch and Ugoji, 2008). Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production (Nameni et al., 2008). Maximum contaminant level for chromium set by Environmental Protection Agency (EPA) drinking water standard is 0.1 mg/L. World health organization recommended the maximum allowable concentration of 0.05 mg/L in drinking water for chromium (VI) (Shah, 2009).

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Several physicochemical wastewater treatment processes have been developed and reported to remove hexavalent chromium. These include chemical reduction followed by precipitation, electrochemical precipitation, ion exchange, solvent extraction, evaporation, reverse osmosis, foam separation, removal, biosorption (Babel and Opiso, 2007; Figueiredo et al., 2010; Nameni et al., 2008).

The ion exchange method using conductive polymer is a frequently used treatment technology for chromium removal. This technology removes chromium ions from the aqueous phase by replacing them with the anion present in the ion exchange resin. Review of the literature showed that among the ion exchange polymers, synthesized polypyrrole in solutions with small dopants such as chloride, perchlorate, and nitrate, mainly exhibit anion-exchanger behavior due to the high mobility of these ions in the polymer matrix. While under certain conditions, the cation exchange behavior has been also found to take place with large dopants such as polyvinylsulfonate and polystyrenesulfonate due to immobility of these ions in the polymer matrix (Deng and Bai, 2004). Removal of metal ions by several functionalized polymers based on amines derivatives such as polyacrylonitrile fibers, ethylenediamine, polyacrylamides, poly-4-vinylpyridine, polyethyleneimine, and aniline formaldehyde condensate has been reported (Pahlavanzadeh et al., 2012; Jeon and Holl, 2003; Katal et al., 2011; Kumar et al., 2007a, 2008b; Viel et al., 2003). Chakraborty et al. have investigated one amine-based polymer, short-chain PAn coated on jute fiber for the removal of chromium in a batch fixed-bed column (Kumar et al., 2008b, 2009c). Polypyrrole has been also used in the removal of fluoride ions from aqueous solution (Karthikeyan, 2009).

A number of statistical methods have been developed for optimizing adsorption process. One-factor at a time is a conventional and classical method that needs to perform a lot of experiments and could not reveal the alternative effects between components. This method is also time consuming and requires a number of experiments to earn optimum conditions, which are invalid (Alam, 2007). In this research, the response surface methodology (RSM) was used to optimize the parameters affecting the sorption of Cr (VI). RSM is a new method that mathematical and statistical techniques will be used in this method for experimental design, model development, and evaluation of parameters and optimization of conditions (Rastegar et al., 2014). Statistical optimization shows the work of each components of the process (Amani et al., 2011). Central composite design (CCD) is applied widely in the second-order response surface models (Anderson and Whitcomb, 2000; Myers and Montgomery, 2002).

The main objective of CCD is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications. There is no information available in

the literature regarding the optimization of chromium removal on PPy. Therefore, we decided to study more thoroughly the phenomenon of removal of chromium in PPy. The effects of operating parameters such as initial feed concentration, temperature; pH, adsorbent dose and contact time were optimized using response surface methodology.

2. Materials and methods

2.1. Materials

All chemicals were used includes ferric chloride and pyrrole were analytical grade reagents. Chromium solutions were prepared in distilled water using $K_2Cr_2O_7$. Pyrrole (Merck) was purified by vacuum distillation for polymerization.

2.2. Sorbent preparation

In order to prepare the polypyrrole, 5g of $FeCl_3$ was added to 100 mL of distilled water and until a uniform solution resulted using magnetic mixer. Then, 1 mL fresh distilled pyrrole monomer was added to the solution and the reaction was carried out for 4 h at room temperature. Then the product was filtered and washed for several times with deionized water and dried at room temperature (Katal et al., 2011). The polymerized pyrrole was used as absorbent for removal of chromium ion.

2.3. Instrumentation

In this study, scanning electron microscope ((SEM) model XL30) was used to characterize the surface of the PPy at very high magnification. The PPy was coated with gold and palladium by a sputter coater with conductive materials to improve the quality of micrograph. The thickness of the coating was 30.00 nm, and the density was 19.32 g/cm^3 . All gravimetric measurements have been done by microdigital scale FR200. The total chromium was determined with atomic absorption spectrophotometer (Model 929, Uni-cam) using an air-acetylene flame at a 429-nm wave-length and a slit width of 0.5 nm. Sensitivity of the spectrophotometer varied with wavelength and slit width. At 429 nm, the detection limit of total chromium was 1–100 mg/L. The Cr (VI) was determined by a colorimetric procedure using a UV spectrophotometer (Varian ModelCary 50) at a 540-nm wavelength with 1,5-diphenylcarbazide method. This method was suitable for the determination of Cr (VI) in the range from 0.10 to 1.0 mg/L (APHA, 1998; Katal et al., 2011).

2.4. Batch adsorption experiments

The adsorption experiments were performed by mixing the different amounts of adsorbent with 100 mL of Cr (VI) ion solution. A magnetic mixer with 400rpm was applied throughout all experiments.

At the end of predetermined time intervals, the sorbate was filtered and the concentration of Cr (VI) ion was determined. All experiments were carried out twice. The Cr (VI) concentration retained in the adsorbent phase was calculated according to Eq. (1).

$$q_t = (C_i - C_e) \times V/m \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of chromium in solution respectively; V is the volume (L) and m is the weight (g) of the adsorbent. Two replicates per sample were done and the average results are presented. By known initial and equilibrium concentrations of chromium, the adsorption efficiency of chromium by PPy can be calculated using Eq. (2).

$$\% \text{ Removal} = (C_i - C_f) / C_i \times 100 \quad (2)$$

2.5. Experimental design and optimization

Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (Sahan 2010; Sahua 2009). In this work using Design-Expert 7.0 a 2^{5-1} fractional factorial design with 6 central points and 10 axial points was selected. In the regression equation, the test variables were coded according to the Eq. (3).

$$X_i = (x_i - x_0) / \Delta x \quad (3)$$

where, X_i is the dimensionless coded value of the i th independent variable, X_0 is the value of X_i at the center point and Δx is the step change value. The behavior of system is explained by the following second-order polynomial empirical model Eq. (4).

$$y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j + \varepsilon \quad (4)$$

where: y is the response, β_0 is the constant coefficient, X_i ($i = 1-5$) are non-coded variables, β_i s are the linear, and β_{ii} s are the quadratic, and β_{ij} s (i and $j = 1-5$) are the second-order interaction coefficients. The residuals for each experiment were computed as in Eq. (5), where, ε_i , y_i and $\hat{y}_i$ are the residual of i th experiment, observed response and predicted response, respectively (Trinh and Kang, 2010).

$$\varepsilon_i = y_i - \hat{y}_i \quad i=1,2,\dots,n \quad (5)$$

Data were processed for Eq. (4) using Design-Expert 7.0 program including ANOVA to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination (R^2), and its statistic significance was checked by the F-test in the same program.

2.6. Column experiments

A glass column with an i.d. of 2 and height of 25 cm was used to column sorption experiments. In

order to providing a uniform feed flow of the aqueous solution until 2 cm of high of column a layer of glass beads with 1.5 mm in diameter was used. Peristaltic pump (pp40, Miclins) was used to pumped Cr (VI) aqueous solution upward through the column at a special flow rate 5 mL/min. Special amount of PPy was located in the column to provide the required bed height of the sorbent. To analysis of metal concentration in the outlet flow samples were obtained at different time. After experiments, distilled water was applied to wash the sorbents in the column until the pH of the wash effluent became near 7.0.

The total amount of metal ions sent to the column can be calculated from the Eq. (6):

$$M_{total} = C_o \cdot F \cdot t_e \quad (6)$$

where: C_o is the inlet metal ion concentration (mg L^{-1}), F the volumetric flow rate (mL min^{-1}) and t_e is the exhaustion time (min).

The total amount of metal sorbed in the column (M_{ad}) is found by the amount of flow rate multiplied by the area above the breakthrough curve (outlet metal concentration versus time). By dividing the metal mass (M_{ad}) by the mass of sorbent (M) will be earned the uptake capacity (Q) of the mass.

Using the ratio of Cr(VI) ions sorbed to sorbent (M_{ad}) to the total amount of Cr(VI) ions sent to the column (M_{total}) total metal removal (%) can be calculated that was showed in the as Eq. (7):

$$\text{Total metal removal \%} = (M_{ad} / M_{total}) \times 100 \quad (7)$$

3. Results and discussion

3.1. Characterization of PPy

The characterization of PPy was based on the last research (Katal et al., 2011). SEM micrograph shows the morphology of the produced polypyrrole and it clearly confirms the formation of irregular polymer regions. Also the structure of produced polymer was also determined by FTIR spectrum. The FTIR spectra were recorded in the region 2500-500 cm^{-1} and are consistent with literature (Rai et al., Song et al., 2004, 2008; Vishnuvardhan et al., 2006). The peak at 1542 cm^{-1} corresponds to typical polypyrrole ring vibration and the peak at 1306 cm^{-1} corresponds to C-H band in-plane vibration. The peak at 1041 cm^{-1} corresponds to in-plane vibration of C-H and N-H, while the peak at 893 cm^{-1} corresponds to C-H out-of-plane vibration (Planche, 1994).

3.2. Development of regression model equation

The five variables include of initial Cr (VI) concentration, pH, adsorbent dose, contact time and temperature were chosen to obtain the optimum levels. A five-factor-five-level CCD design was used to determine the optimal values for the factors. The

ranges and the levels of the variables investigated in this study are listed in Table 1.

Once the desired value ranges of the variables had been defined, they were coded to lie at ± 1 for the factorial points, 0 for the center points, and $\pm \alpha$ for the axial points. In this case a central composite design (fractional) for five independent variables each at five levels was employed to fit the model in which 32 experiments were required for this procedure.

The CCD is shown in Table 2, which reveals the experimental conditions and their response. The model equation for coded values in quadratic model fitting the experimental results was presented in Eq. (8).

$$\begin{aligned} \text{Chromium removal (\%)} = & +64.90 - 14.13 X_1 + 2.71 X_2 \\ & + 2.46 X_3 - 1.37 X_4 + 1.21 X_5 - 3.65 X_1^2 - 0.65 X_2^2 + 1.48 X_3^2 \\ & + 1.10 X_4^2 + 0.98 X_5^2 \end{aligned} \quad (8)$$

The ANOVA for the reduced quadratic model is shown in Table 3. The F-value for the model shows that model is significant at less than a 0.05% level (i.e. at 95% confidence interval).

3.3. Statistical analysis

Eq. (6) has been used to visualize the effects of experimental factors on conversion percentage response in Figs. 1–5. Fig. 1 shows the actual and the predicted removal of chromium percent.

Table 1. Experimental range and levels of the independent test variables

Variable	Low axial ($-\alpha = -2$)	Low factorial (-1)	High factorial (+1)	High axial ($+\alpha = +2$)
pH	3	5.25	9.75	12
Time(min)	2	6.5	15.5	20
Adsorbent dose(g)	0.1	0.325	0.775	1
initial conc.(mg/L)	150	187.5	262.5	30
Temperature($^{\circ}\text{C}$)	25	32.5	47.5	55

Table 2. Experimental design matrix and results

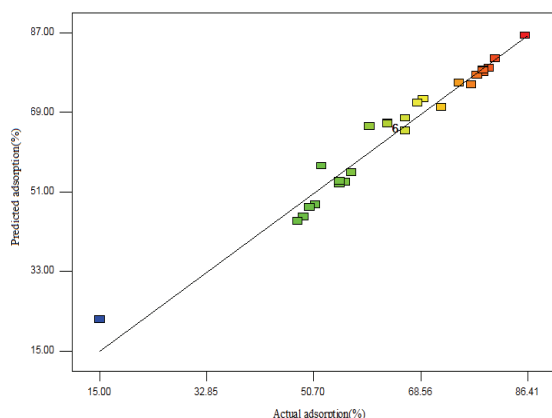
Run	pH	Time (min)	Absorbent dose(g)	Initial conc. (mg/L)	Temperature ($^{\circ}\text{C}$)	Removal (%)
1	9.8	6.5	0.8	187.5	47.5	55
2	7.5	11.0	0.1	225.0	40.0	60
3	7.5	11.0	0.6	225.0	25.0	63
4	9.8	6.5	0.3	262.5	47.5	48
5	7.5	11.0	0.6	225.0	40.0	66
6	7.5	11.0	0.6	225.0	40.0	66
7	7.5	11.0	0.6	225.0	40.0	66
8	7.5	20.0	0.6	225.0	40.0	66
9	5.3	15.5	0.3	187.5	32.5	80
10	9.8	15.5	0.3	262.5	32.5	51
11	7.5	11.0	0.6	225.0	40.0	66
12	12.0	11.0	0.6	225.0	40.0	15
13	7.5	11.0	0.6	225.0	40.0	66
14	9.8	6.5	0.3	187.5	32.5	49
15	9.8	15.5	0.3	187.5	47.5	56
16	5.3	6.5	0.8	262.5	47.5	78
17	7.5	11.0	0.6	150.0	40.0	69
18	7.5	2.0	0.6	225.0	40.0	52
19	9.8	15.5	0.8	187.5	32.5	55
20	5.3	6.5	0.3	262.5	32.5	72
21	7.5	11.0	0.6	225.0	40.0	66
22	9.8	15.5	0.8	262.5	47.5	57
23	7.5	11.0	1.0	225.0	40.0	75
24	7.5	11.0	0.6	300.0	40.0	63
25	5.3	15.5	0.8	187.5	47.5	86
26	5.3	15.5	0.8	262.5	32.5	81
27	7.5	11.0	0.6	225.0	55.0	68
28	9.8	6.5	0.8	262.5	32.5	50
29	5.3	6.5	0.8	187.5	32.5	79
30	3.0	11.0	0.6	225.0	40.0	79
31	5.3	6.5	0.3	187.5	47.5	77
32	5.3	15.5	0.3	262.5	47.5	79

Table 3. Analysis of variance (ANOVA) for response surface quadratic model applied for the removal of Cr (VI)

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F	Remarks
Model	5772.901	20	288.645	13.789	< 0.0001	Significant
A-pH	4788.375	1	4788.375	228.69	< 0.0001	Significant
B-Time(min)	176.0417	1	176.0417	8.407753	0.0145	Significant
C-Adsorbent dose(g)	145.0417	1	145.0417	6.927192	0.0233	Significant
D-initial conc.(mg/L)	45.375	1	45.375	2.167111	0.1690	
E-Temperature(°C)	35.04167	1	35.04167	1.673591	0.2223	

In Fig. 1, the values of R^2 and R^2_{adj} were found to be 0.96 and 0.89, respectively. The same figure proves that actual and the predicted removal of chromium percent is well in agreement with the observed ones. Table 3 gives an understanding into the linear, quadratic and interaction effects of the factors.

These analyses were performed by Fisher's 'F' and Student's 't' tests. The Student's 't' test was applied to find the importance of the regression coefficients of the factors. The p value is applied as a tool to evaluate the importance of factors and interaction between different factors. Generally, the larger magnitude of t and smaller value of p, the more significant is the corresponding coefficient term (Mason, 2003; Trinh and Kang, 2010). In this work pH, contact time, adsorbent dose (linear) and pH (quadratic) with confidence interval (C.I.) of 95% were found to have significant effects on the removal of chromium, with pH imposing the greatest effect on the removal of chromium.

**Fig. 1.** The actual and predicted plot of removal of chromium (VI)

3.4. Removal capacity of chromium (VI)

Response surface methodology was used to investigate the effects of the five factors on the removal of chromium, and three-dimensional plots were drawn. Figs. 2-5 show the removal of chromium percent response surface graphs.

It can be clear from Fig. 2 that there is a combined effect of pH and contact time on removal of Cr (VI) at constant initial concentration (225 mg/L), temperature (40°C) and adsorbent dose (0.6 g). It can be also seen that the maximum removal of chromium >79% was determined at constant pH (5.3) and contact time (15 min).

Fig. 3 illustrates the effect of temperature and pH on Cr (VI) removal at constant initial concentration of Cr (VI) (225 mg/L), adsorbent dose (0.6 g) and contact time (11 min). Temperature increasing from 32.5 to 47.5 °C has positive effect on the removal of Cr (VI) ions from aqueous solution. The increase in metal uptake with increasing temperature may be due to either higher affinity of sites for metal or an increase in number of binding sites on PPy. It is clear from this figure that the removal percent of Cr (VI) decreases with increase in pH from 5.3 to 9.8. It is important that the maximum removal at all the concentrations takes place at pH 5.3. A maximum removal of chromium >79% was determined at pH (5.3) and temperature (47.5°C). The effect of initial pH and initial chromium ion concentrations on the removal of the Cr (VI) is shown in Fig. 4.

The metal removal increased with decrease of initial solution pH ranging from 9.8 to 5.3 as well as with initial metal ion concentration ranging from 262.5 to 187.5 mg/L. An increase of metal removal by increasing initial metal ion concentration is a result of the increase in the driving force of the concentration gradient, rather than increase in the initial metal ion concentration.

Maximum removal of chromium >79% was determined at constant pH (5.3) and initial concentration of Cr (VI) (187 mg/L), constant adsorbent dose (0.6 g), temperature (40 °C) and contact time (11min). The interactive effect of temperature and initial concentration of Cr (VI) in the solution on removal percent of Cr (VI) onto PPy is studied. This condition show that removal decreases with increasing metal concentration up to 150–250 mg/L. A maximum removal of chromium >70% was determined at constant pH (7.5), adsorbent dose (0.6 g), contact time (11 min), temperature (47°C) and initial concentration (187 mg/L). Fig. 5 shows the three-dimensional response surfaces which were constructed to show the most important two variables (pH and adsorbent dose) on the removal of chromium(VI) at constant temperature (40 °C), initial concentration of Cr(VI) (225 mg/L) and contact time (11min).

The higher values of chromium ions uptake obtained by the decrease in biomass dosage and increase in initial solution pH simultaneously. This may be explained by the increase in availability of binding sites at higher initial solution pH and this improved in the access of metal ions to the metal-binding sites of cell wall (Lu et al., 2006). A

maximum removal of chromium >80% was determined at constant temperature (40°C) and initial concentration of Cr (VI) (225 mg/L). The combined effect of temperature and Adsorbent dose on removal of chromium (VI) at constant pH (7.5), initial concentration (225 g/L) and contact time (11min) is studied. A maximum removal of chromium >75% was determined at temperature (47°C) and Adsorbent dose (0.7 g). The three dimensional response surfaces of the combined effect of adsorbent dose and contact time on removal of Cr(VI) at constant initial concentration (225 mg/L), temperature (40°C) and pH (7.5) is studied. A maximum removal of chromium >70% was determined at a contact time of 15 min and for an adsorbent dose of 0.7 g.

3.5. Determination of optimum conditions

Find of optimum process parameters to maximize the removal of chromium from the developed mathematical model equations was aim of this study. The quadratic model equation was used within the experimental range studied.

The optimum removal conditions were temperature 47.5°C, initial feed concentration of Cr (VI) 187.5 mg/L, pH 5.3, adsorbent dose 0.8 g and contact time 15.3 min. Use this program to help optimize your product or process. This software provides highly efficient design of experiments (DOE). The desirability of the process optimization was found to be 1.00 and the value is completely dependent on how closely the lower and upper limits are set relative to the actual optimum.

3.6. Confirmatory experiments

Model validations had been determined at five experimental combinations was used for validation of the statistical model. The results of analysis indicated that the experimental values were in good agreement with the predicted ones (Table 4). Under these optimized conditions (row =1 in table 4), the predicted response for removal chromium was 85.96%, and the observed experimental value was 90.1%.

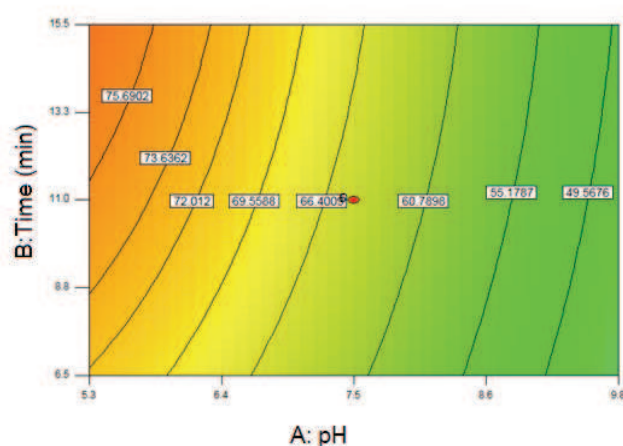


Fig. 2. The combined effect pH and contact time on removal of chromium (VI) at constant initial concentration (225 mg/L), temperature (40°C) and Adsorbent dose (0.6 g)

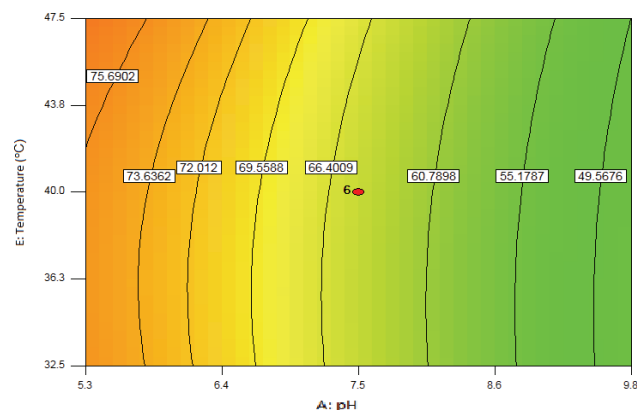


Fig. 3. The combined effect of temperature and pH on removal of chromium (VI) at constant initial concentration of Cr(VI) (225 mg/L), adsorbent dose (0.6 g) and time (11 min)

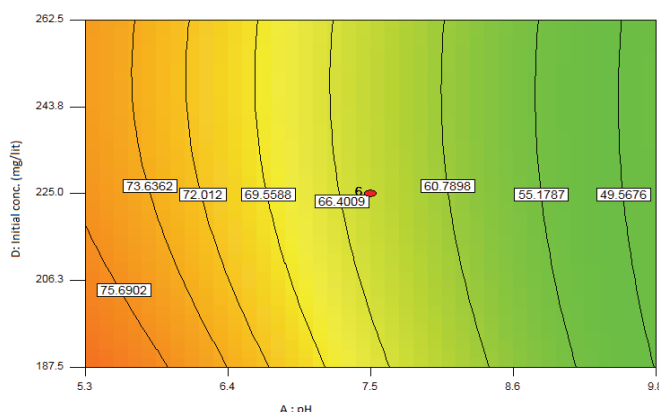


Fig. 4. The combined effect of initial concentration of Cr (VI) and pH on removal of chromium(VI) at constant adsorbent dose (0.6 g), temperature (40 °C) and time (11 min)

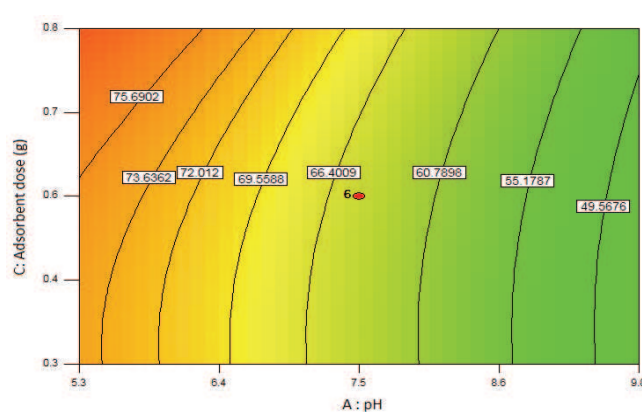


Fig. 5. The combined effect Adsorbent dose and pH on removal of chromium (VI) at constant initial concentration (225 mg/L), temperature (40°C) and time (11 min)

These results confirmed the validity of the model, and the experimental values were determined to be quite close to the predicted values.

3.7. Kinetics of sorption

Three kinetic equations (Morris–Weber, Lagergren and pseudo second order) were used for evaluation of kinetic data of sorbed Cr (VI) onto PPy. To study the change in the concentration of sorbate in aqueous solution onto sorbent with contact time, the kinetic data of Cr (VI) sorption onto PPy was fitted to Morris–Weber, Eq. (9) (Hossini et al., 2014).

$$q_t = K_{id}(t)^{0.5} + C \quad (9)$$

where: q_t is the sorption capacity of sorbent at time 't'. The values of rate constant of intraparticle transport, K_{id} and correlation factor, R^2 are illustrated in Table 5. The Pseudo first order equation of the Cr (VI) sorption onto PPy was tested by fitting the data to the linear form of Lagergren equation, to find the rate constant of Lagergren equation for sorption for Cr (VI) – PPy system.

$$\log(q_e - q_t) = \log q_e - (K/2.303)t \quad (10)$$

where q_e is the sorption capacity at equilibrium and K_1 is the first order rate constant.

The rate constant the sorption capacity at equilibrium and correlation factor of Cr (VI) sorption onto PPy are shown as in Table 5. The Cr (VI) sorption onto PPy kinetic data was tested by pseudo - second order (Eq. 11) (Pandey et al., 2010):

$$t/q_t = 1/(Kq_e^2) + t/q_e \quad (11)$$

The constant of pseudo-second order equation was calculated from the slope of the straight line and the value of rate constant, sorption capacity at equilibrium and correlation factor are presented in Table 5. Based on the results in Table 5 (correlation factor), Cr (VI) sorption onto PPy can be described by pseudo second order equation.

3.8. The isotherm model

3.8.1. The Langmuir isotherm model

The Langmuir model uses for monolayer sorption onto surface of sorbent containing finite amount of identical sorption sites which is indicated by the following Eq. (12) (Brinza et al., 2007):

$$q_e = (q_m K_L C_e) / (1 + K_L C_e) \quad (12)$$

where q_e is the amount of Cr (VI) sorbed per specific amount of sorbent (mg/g), C_e is equilibrium concentration of Cr(VI) in the aqueous solution (mg/L), and q_m is the maximum sorption capacity for Cr(VI) sorption to PPy that required to form a monolayer (mg/g). The Langmuir equation can be

presented to linear form for the convenience of plotting and calculating the Langmuir constants (K_L). The values of q_m and K_L can be calculated from the linear plot of C_e/q_e versus C_e (Eq. 13).

$$C_e/q_e = 1/(q_m K_L) + 1/q_m \cdot C_e \quad (13)$$

The equilibrium data of Cr(VI) sorption onto PPy were evaluated by the linearized form the Langmuir sorption isotherm Eq. (13). The Langmuir constants, K_L and monolayer sorption capacity, q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e (Fig.6). The results of fitting the equilibrium data to Langmuir isotherm are shown that values of q_m and K_L are 32.25 and 0.01 respectively and the R^2 is 0.99 (Malakootian et al., 2008).

3.8.2. The Freundlich isotherm model

Freundlich isotherm assumes that the uptakes of adsorbate occur on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by Eq. (14).

$$q_e = K_F (C_e)^{1/n} \quad (14)$$

where K_F is, roughly, an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. Equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of $\log q_e$ versus $\log C_e$ based on experimental data.

A linear form of the Freundlich expression will yield the constants K_F and $1/n$ Eq. (15).

$$\log(q_e) = \log(K_F) + 1/n \log(C_e) \quad (15)$$

The slope and the intercept correspond to $(1/n)$ and K_F , respectively. It was revealed that the plot of $\log q_e$ and $\log C_e$ yields a straight line (Fig.7).

The results of fitting the equilibrium data onto Freundlich isotherm are presented that values of n and K_F are 1.5 and 0.89 respectively and the R^2 is 0.999 (Malakootian et al., 2008; Mousavi and Seyedi, 2010).

3.8.3. The Dubinin–Radushkevich isotherm model

The Dubinin–Radushkevich (D–R) (Ghazy and Ragab, 2007) isotherm is valid at low concentration ranges and can be used to describe adsorption on both homogeneous and heterogeneous Surfaces. The linear form of this model is expressed by Eq. (16):

$$\ln(q_e) = \ln(q_m) - \beta \epsilon^2 \quad (16)$$

where: q_e is the amount of Cr (VI) adsorbed per unit of the adsorbent (mg/g), q_m is the monolayer capacity, and β is the activity coefficient related to mean

sorption energy and ε is the Polanyi potential described as Eq. (17):

$$\varepsilon = RT \ln [1 + (1/C_e)] \quad (17)$$

From the plots of $\ln q_e$ versus ε^2 (Fig. 8) the values of β , q_m were calculated by the slope and intercept of the linear plot. The results are indicated that values of q_m and β are 14.9 and 9×10^{-5} respectively and the R^2 is 0.946. Based on our results, equilibrium data of sorption of Cr (VI) from aqueous solution to PPy can be presented by Freundlich isotherm equation.

3.9. Comparison between conductive polymers

The comparison of sorption capacities between different types of conductive polymers are presented in Table 6. It is clear that, the sorption capacity of PPy is higher than others kinds of conductive polymers, PPy has also a considerable potential for the Cr (VI) removal from aqueous solution.

3.10. Application of PPy for removal of the Cr (VI) from Tannery wastewater

For understanding of PPy ability for Cr(VI) removal from, a bulk wastewater sample was collected from a local wastewater (Shahi, Iran). The pH and initial concentration of the wastewater were determined at the beginning of sorption experiments, and are presented in Table 7.

Sorption process was done on 100 mL of wastewater with PPy dose of 0.8 g. The suspensions were stirred at room temperature (20 °C) and 200 rpm. Table 7 indicates Cr (VI) removal efficiency from wastewater. As can be seen, PPy is an efficient adsorbent for the removal of Cr (VI) from industrial wastewater.

3.11. Column study

3.11.1. Effect of bed height

Fig. 9 showed the sorption breakthrough curves obtained for Cr(VI) sorption onto PPy at 50mg/L initial Cr (VI) concentration and at different bed heights from 5 to 20 cm at 5mL/min flow rate. The results show with increase that bed height from 5 to 20 cm the volume of treated solution (V_{eff}), the both breakthrough time (t_b) and exhaustion time (t_e) was increased.

Table 4. Model Validation

pH	Time(min)	Adsorbent dose(g)	Initial conc.(mg/L)	Temperature, X_1 , (°C)	Adsorption of Cr (VI), (%)	
					Predicted	Experimental
5.3	15.4	0.8	187.5	46.6	85.96	90.1
5.3	14.0	0.8	187.8	47.5	85.61	88.3
5.3	14.4	0.8	187.5	47.5	85.45	84.6
5.5	15.5	0.8	187.5	47.5	85.45	87.6
5.3	15.3	0.8	207.5	47.5	84.72	81.3

Table 5. Kinetic constants for the adsorption of Cr (VI) onto ppy at different initial concentration parameters

Kinetic equation/ Parameters	Morris and Weber					Pseudo first order					Pseudo second order				
C_0 (mg/L)	150	175	200	250	300	150	175	200	250	300	150	175	200	250	300
K_{id}	0.37	0.45	0.54	0.73	0.95										
K_1						0.08	0.08	0.08	0.08	0.08					
K_2											0.09	0.07	0.06	0.04	0.03
q_e (mg/g)						1.79	2.18	2.6	3.52	4.5	8.9	10.41	11.7	14.7	17.5
R^2	0.98	0.98	0.98	0.98	0.98	0.96	0.96	0.96	0.96	0.96	0.99	0.99	0.99	0.99	0.99

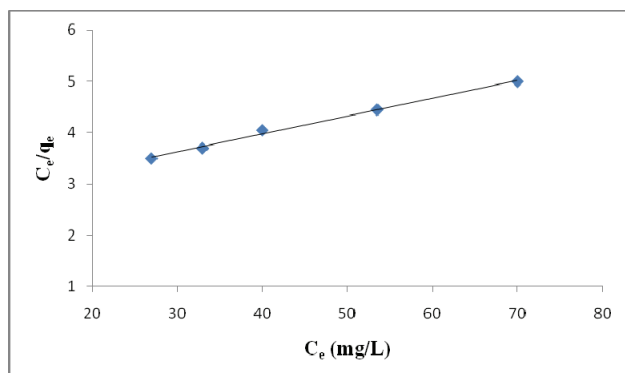


Fig. 6. Langmuir sorption isotherm of Cr (VI) onto PPy

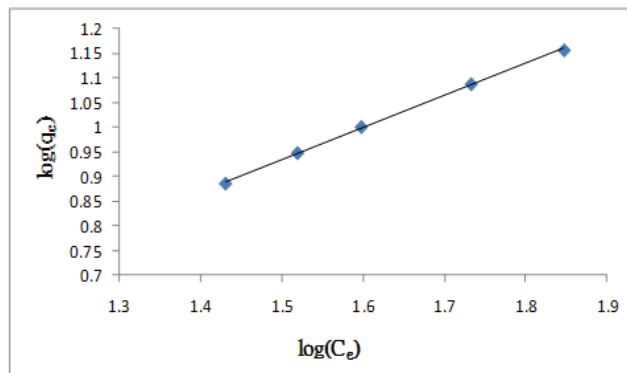


Fig. 7. Freundlich sorption isotherm of Cr (VI) onto PPy

Table 6. Comparison between conductive polymers

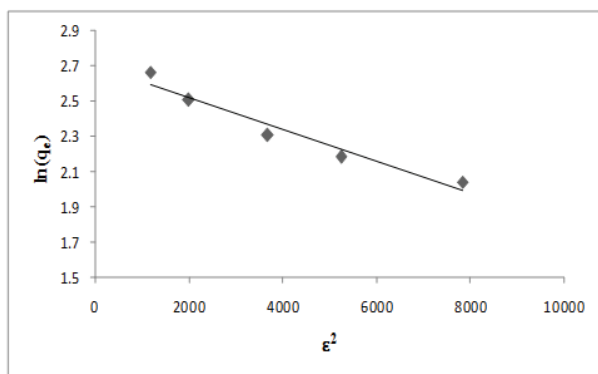
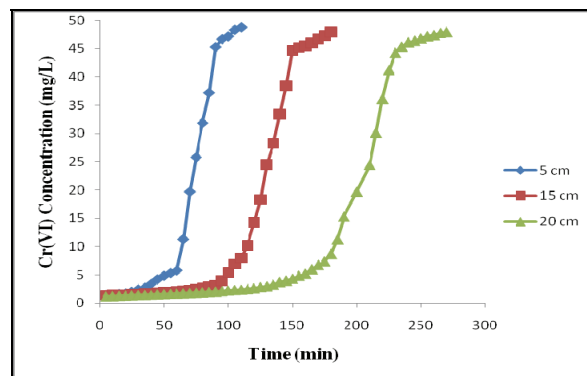
Conductive polymer	Adsorption capacity(mg/g)	References
PPy	21	In this research
Polyaniline	3.1	Eisazadeh (2007)
Poly3-Methyl Thiophene	2.2	Ansari and Delavar (2010)
Polyaniline coated on the fiber	10.5	Kumar et al. (2008)

Table 7. Application of PPy for the removal of Cr(VI) from real wastewater

Wastewater	Initial concentration (mg/L)	pH	Removal efficiency (%)
Tannery	85.3	4.97	88.5

Table 8. Column data and parameters obtained at different bed heights

Bed Height	$t_b(\text{min})$	$t_e(\text{min})$	$M_{\text{total}}(\text{mg})$	$M_{\text{ad}}(\text{mg})$	$q(\text{mg/g})$	Removal efficiency %
5 cm	60	110	27.5	19.32	19.32	70.25
15 cm	115	180	45	32.12	20.07	71.37
20 cm	180	270	67.5	51.78	23.53	76.71

**Fig. 8.** D-R sorption isotherm of Cr (VI) onto PPy**Fig. 9.** Breakthrough curves for Cr(VI) sorption onto PPy at different bed heights (inlet Cd(II) concentration: 50 mg L⁻¹, flow rate 5 mL min⁻¹, pH: 3)

Further, it was observed that the percentage removal efficiency and the sorption capacity increased with the increase in bed height that is due to an increase in the adsorbent doses in larger beds which provided more sorption sites for the binding of metal ion. Also the increase in bed height from 5 to 20 cm increased the breakthrough time (Table 8)

3.11.2. Effect of flow rate

In the continuous study of metal removal from water and wastewater on an industrial scale, investigation of flow rate effect is one of the important parameters (Ko et al., 2000). The effect of different flow rates was investigated by varying the flow rate from 5 to 15 mL/min at the constant bed height (5 cm) and initial Cr (VI) concentration (50 mg/L) that was shown in Fig. 10.

In the low flow rate, initially the adsorption process was very rapid those was due to availability of reaction sites of inside cells and therefore capture metal ions around. In the next stage of the process the uptake becomes less effective because of the gradual occupancy of these sites. When the flow rate is increased with which the break point time and adsorbed ion concentration decreases, the breakthrough curve becomes steeper. The reason is

because the solute resides for more time in to the column due to the more availability of the sorption sites and the more diffusion of the metal ions into the sorbent mass (Malkoc and Nuhoglu, 2006; Villarreal et al., 2011; Vijayaraghavan et al., 2005). The maximum uptake, which was 23.53 mg/g for Cr (VI) was found at the maximum bed depth i.e. 20 cm. that the residence time is not long enough to receive adsorption equilibrium at specified flow rate and the Cr(VI) solution leaves the column before adsorbed (Esfandian et al., 2013; Malkoc and Nuhoglu, 2006; Villarreal et al., 2011). Thus, the contact time of Cr (VI) ions with PPy is not enough at higher flow rate and therefore removal efficiency was decreased.

An earlier breakthrough and exhaustion time were observed in the sorption process, when the flow rate was varied from 5 to 15 mL/min. The uptake capacity of PPy was obtained 19.32 mg/g for flow rate 5 mL/min, 17.12 mg/g for flow rate 10 mL/min and 14.06 mg/g for bed height 15 mL/min. The sorption data were evaluated and the total sorbed quantities, removal percents and maximum Cr (VI) uptakes with respect to flow rate are presented in Table 9. According to Table 9, in general the total sorbed Cr (VI) quantity, percentage of Cr(VI) removal and maximum Cr (VI) uptake decreased

when flow rate increased. Maximum values of total sorbed Cr(VI) quantity 19.32 mg, maximum Cr(VI) uptake 19.32 mg/g and Cr(VI) removal percentage 70.25 %, were obtained at 5 mL/min flow rate.

3.11.3. Effect of initial metal ion concentration

Fig. 11 showed the effect of initial metal ion concentrations on the sorption of Cr(VI) onto PPy at a constant bed height of 5 cm and flow rate 5 mL/min. As it showed, increasing initial metal ion concentration caused the increasing concentration of treated solution increased and the breakthrough exhaustion time decreased. This indicated that higher treated volumes of effluents were obtained at lower inlet metal ion concentration. This can be explained that the lower concentration of Cr(VI) in aqueous solution caused a slower transport of metal ions

because of diffusion coefficient decreasing (Esfandian et al., 2013). High metal ion concentrations lead to the rapid saturation of the sorbent bed which this phenomena leads to the earlier breakthrough and exhaustion time.

3.11.4. Treatment of industrial wastewater in column mode

In order to facilitate large scale application, the PPy was employed for the treatment of industrial wastewater (tannery wastewater) in a continuous column mode and their reusability was assessed.

Fig. 12 shows the breakthrough curves for the sorption. The t_e , t_b , q (mg/g), M_{total} , M_{ad} and removal efficiency are shown in the Table 10. As can be seen, the PPy show considerable ability for the removal of Cr (VI) from industrial wastewater.

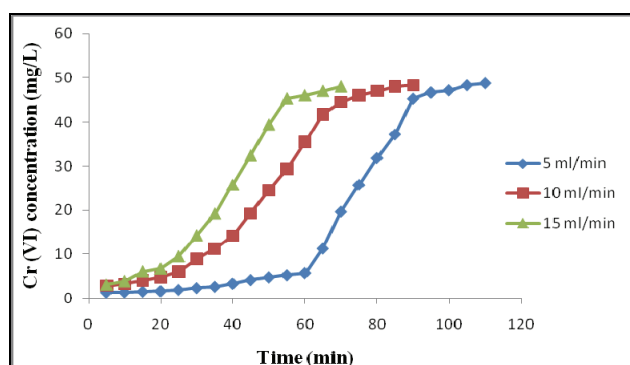


Fig. 10. Breakthrough curves for Cr(VI) sorption onto PPy at flow rates (inlet Cr(VI) concentration: 50 mg L⁻¹, bed height: 5 cm, pH: 3.0)

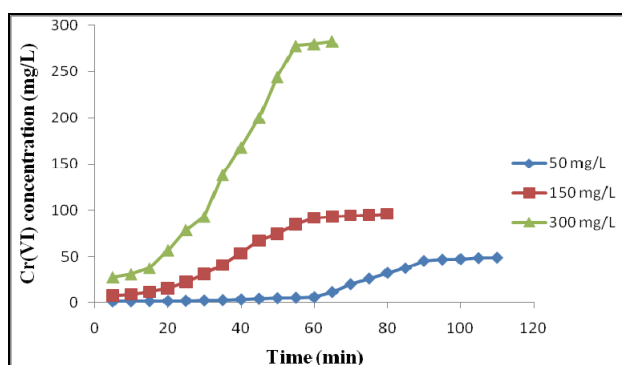


Fig. 11. Breakthrough curves for Cr(VI) sorption onto PPy at flow rates (flow rate: 5 mL min⁻¹, bed height: 5 cm, pH: 3.0)

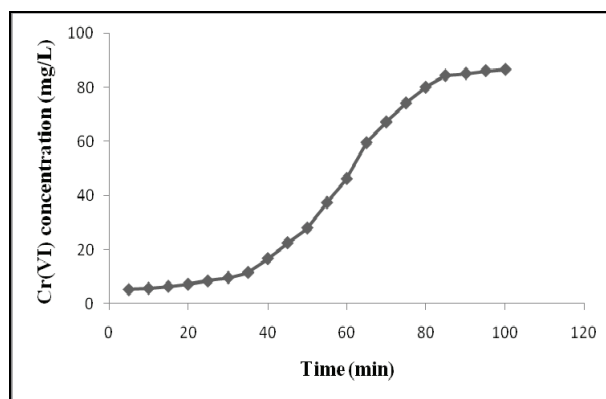


Fig. 12. Breakthrough curves for Cr(VI) sorption onto PPy from industrial wastewater (Bed height: 5 cm, flow rate: 5 mL min⁻¹, inlet cadmium concentration in the industrial wastewater: 87 mg L⁻¹)

Table 9. Column data and parameters obtained at different bed heights

Flow rate	t_b (min)	t_e (min)	M_{total} (mg)	M_{ad} (mg)	q (mg/g)	Removal efficiency %
5 mL/min	60	110	27.5	19.32	19.32	70.25
10 mL/min	30	90	45	27.14	17.12	60.31
15 mL/min	20	70	52.5	28.12	14.06	53.56

Table 10. Sorption process parameters for Tannery wastewater

Concentration	t_b (min)	t_e (min)	M_{total} (mg)	M_{ad} (mg)	q (mg/g)	Removal efficiency %
85.3 (mg/l)	35	100	43.5	27.2	27.2	62.52

4. Conclusions

This work has demonstrated the application of RSM in seeking optimize the chromium (VI) removal capacity of a new adsorbent PPy. The optimum conditions for removal of Cr (VI) were evaluated as pH 5.3, temperature 46.5°C, initial chromium (VI) concentration 187.5 mg/L, Adsorbent dose 0.8 g and contact time 15.4 min by utilization of RSM. Under these optimum conditions, maximum removal amount of Cr (VI) ion was obtained as 89.3%. From the statistical analysis (ANOVA table), the Adsorbent dose, pH, contact time have significant effects on the chromium (VI) removal.

The results of a confirmation experiment were found to be in good agreement with the values predicted by the model. This demonstrates that to obtain a maximum amount of information in a short period of time, with the least number of experiments, RSM and CCD can be successfully applied for modeling and optimizing the adsorption process.

The Langmuir, Freundlich and Dubinin–Radushkevich isotherms are subjected to sorption data to estimate sorption capacity, intensity and energy. The results gained from this study were well described by the theoretical Freundlich. Three equations, i.e. Morris–Weber, Lagergren and pseudo second order have been tested to track the kinetics of adsorption process. The results gained from this study were well described by the theoretical pseudo second order. Also, the comparison between different conductive polymers had been studied that PPy has highest adsorption capacity between them.

The Cr (VI) removal in the continuous mode was studied. Effect of different parameter such as effect of flow rate, bed height and initial concentration were investigated. The results show that an increase in the bed height increases the q (mg/g) and removal efficiency but flow rate and initial concentration increase reduce the removal efficiency and q (mg/g). Meanwhile the treatment of tannery wastewater in the column mode by PPy was studied that the results was considerable.

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DISTRIBUTION OF HEAVY METALS IN THE LAKE TALKŠA (LITHUANIA) SAPROPEL AND POSSIBILITIES OF PRACTICAL USE

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Abstract

This article presents the results of investigations addressing the accumulation of heavy metals in different layers of the Lake Talkša, Lithuania. For the sampling from the ice of intact structure of the sediment the turf borer was used. Concentrations of these heavy metals in sapropel layers were determined in the extracts of sapropel. After the preparation of samples, the concentration of Pb, Ni, Cr, Zn and Cu were measured in the laboratory by means of atomic absorption spectrometry. The results showed that sapropel taken from the northern shores of Talkša Lake is stratified according to LAND 20-2005 and should be classified as sludge of I and II category. Based on the concentration of Pb, Ni, Zn, Cu, sapropel should be classified as I category. However, according to the maximum concentrations of Cr (257.5 mg/kg) detected in the upper horizon of the sludge, sapropel should be considered as of IInd category. Within other horizons, sapropel is not contaminated with heavy metals, while metal concentrations could be treated as trace elements. Sapropel recovered from this part of the lake could be exploited by excavation and widely used for various economic needs.

Key words: heavy metals, lake sediments, purification of lake, sapropel

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1. Introduction

Most chemical elements released into environment are accumulated in soil and in the bottom sediments (or sapropel) of water reservoirs (Baltrėnas et al., 2009; Minkina et al., 2014). Heavy metals enter water reservoirs from atmosphere and during surface water and groundwater infiltration, then reaching the lake sediments (Bai et al., 2011). Pollution with trace elements is regarded as a serious threat to the environment due to pollutants' toxicity, environmental persistence and the ability to be incorporated into food chains (Gao et al., 2013).

Part of heavy metals, which are found in deeper deposits of sapropel, are accumulated naturally in the course of complex hydro-chemical and hydro-biological processes over thousands of years, when the atmosphere and waters were not as

polluted as they are today. With the intense urbanization and development of industrial and agricultural activities, the extent of trace element accumulation has grown (Gao et al., 2013; Huo et al., 2014). The chemical and biogenic composition of the built up sapropel differ, depending on lake background and the type of eutrophication. Mineral composition of sapropel determines its use.

Lithuania has about 2,850 lakes, each covering over 0.5 hectare and around 3,150 lakes of under 0.5 hectare each. In total, they cover a territory of 91,360 hectares (Kilkus, 2005). Eutrophication causes lakes quality to decline, since they accumulate sludge, while lakeshores get covered with excess vegetation. Consequently, all this entails a serious ecological problem.

Although the process of declining lakes may be natural, the anthropogenic contamination adds to a

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fast-paced silting up of lakes (Kozlovskā-Kędziora and Petraitis, 2011; Žvironaitė et al., 2002).

According to many scientists, sapropel or lake silt, which accumulated in natural environment, is unique and valuable sediment (Knicker and Hatcher, 2001; Rohling et al., 2004). It is a complex matter of organic and mineral origin and mostly consisting of the remains of plankton, benthos, algae and other hydrophytes that have stratified with particles of sand, clay and limestone (Capozzi and Picotti, 2003; Menzell et al., 2003). Sapropel is found in Lithuania at the bottoms of lakes and swamps. According to the data by Katkevičius and other researchers (1998), Lithuanian lakes and swamps store approximately 10 billion cubic meters of sapropel of 7–15 m-thick deposits, which have built up over thousands of years and preserve naturally balanced minerals (Ciūnys et al., 1994).

According to its origin, sapropel may be organic or mineral-carbonaceous with pH 6.0–7.5. Its dry matter may include 79.8–90.8 % of organic substances, 2.27–3.56% of nitrogen, 0.56–1.18% of calcium, 0.9–0.15% of P_2O_5 , and 0.055–0.2% of K_2O . Sapropel may include microelements and metals such as Al, Ca, Co, Cu, Fe, K, Mo, Zn, Se, C, J, N, P, S, Si and many more. The organic part of lake sediment is rich in biologically active substances and vitamins, especially those of B group, also enzymes, indispensable amino acids, antibiotics, carbohydrates, estrogens, humic acids, growth stimulators for lipid fractions and other bio-stimulators and probiotics (Katkevičius et al., 1998; Bakšienė, 2009). Because of chemical and physical properties, sapropel is advisable to be used as fertilizer, feed additive, in chemical industry, medicine, as well as energetics (Kozlovskā-Kędziora and Petraitis, 2011).

The composition of the sediment sequences provides the best natural achieves of recent

environmental changes (Olubunmi and Olorunsola, 2010; Nasir and Harikumar, 2011).

The aim of our work was to study the content of heavy metals available in sapropel of Talkša Lake and the change of this content with depth, so as to determine whether such a composition of sapropel is suitable for economic use.

2. Materials and methods

Lake Talkša is located one kilometer from the center of Šiauliai town. The lake covers 56.2 hectares, being 2 km long, while its maximum width reaches 550 m. The northern part of Lake Talkša is connected with Lake Ginkūnai, covering 16 hectares via 150 m-long and 5 m-wide Kulpė canal covered with reed. Overgrowth of vegetation covers almost the whole lake shoreline. Sapropel samples were taken from the northern part of Talkša Lake, this part of the lake showed the largest pollution with chromium (Frisk et al., 2004). Three bores (Fig. 1) were made during field works (2010, February). The coordinates of sampling is given in Table 1.

Table 1. Coordinates of sampling bores made in Talkša Lake

Bore	Coordinates
1	55°56'40.65"N, 23°20'16.00"E
2	55°56'41.34"N, 23°20'24.15"E
3	55°56'65.10"N, 23°20'32.00"E

Samples from the bores were collected at depths of 10 cm. Bottom sediment bores were carried out in the depth of up to 270 cm into the sediment layer. Samples from the same sediment depth were homogenized into a representative sample 27 samples from one bore have been collected and analyzed. Samples of bottom sediment were taken using the drill of turf type.



Fig. 1. Places of bores in Talkša Lake

Quantity of heavy metals of sapropel were measured with *Buck Scientific 210 VGP* Atomic Absorption Spectrophotometer after ash burning and mineralizing in HNO_3 (65%): H_2O_2 (37%) (10 ml:2ml) extraction solution with ETHOS mineraliser (*Milestone*).

Total carbon content (TC) and inorganic carbon (IC) was determined using a total carbon analyzer *TOC-V* by *SHIMADZU*. Total and inorganic carbon in all sapropel samples was measured directly using a total carbon analyzer, while content of organic carbon was found in an indirect way from the difference of measured values of total carbon and inorganic carbon. pH of sediments was measured in 0.01 M CaCl_2 solution using pH meter *pH 538 WTW*. The 15 g of sapropel was diluted with 75 ml of CaCl_2 solution, shaken for 1 hour and measured.

For the assessment of statistical parameters of obtained results, the statistical package *Statistica* has been used. Cluster analysis was performed to classify elements of different sources on the basis of their similarities using dendrograms and to identify relatively homogeneous groups of variables with similar properties.

According Council Directive 86/278/EEC (EC Directive, 1986) member states shall regulate the use of sludge in such a way that the accumulation of heavy metals in the soil does not lead to limit value (Table 2). The purpose of this Directive is to regulate the use of sewage sludge in agriculture in such a way as to prevent harmful effects on soil, vegetation, animal and man, thereby encouraging the correct use of such sewage sludge.

Table 2. Limit values for heavy-metal concentrations in sludge for use in agriculture

Parameters	Limit values
Cd	20 to 40
Co	1000 to 1750
Ni	300 to 400
Pb	750 to 1200
Zn	2500 to 4000
Hg	16 to 25

Impurity of sediments in Lithuanian lakes is usually measured according to the requirements for the use of sludge wastewater for fertilization and recultivation set in LAND 20-2005 (2005) (Table 3). The requirements of Lithuanian Laws are stricter there fore obtained results are compared with these one.

Table 3. Maximum limit values for concentration in sludge

Sludge category	Quantities of Heavy Metal, $\text{mg}\cdot\text{kg}^{-1}$				
	Pb	Ni	Cr	Zn	Cu
I	≤ 140	≤ 50	≤ 140	≤ 300	≤ 75
II	140-750	50-300	140-400	300-2500	50-1000
III	> 750	> 300	> 400	> 2500	> 1000

With reference to LAND 20-2005 (2005), the sludge which can be used for fertilization and recultivation of quarries is classed as I-II category sludge. It is forbidden to use the sludge of III category as fertilizer in the areas intended to be used for vegetables and fruit trees cultivation, but it is allowed to grow field crops within one year after the promulgation on the sowing surface. In case of intention to fertilize the soil with the sludge of II-III category for the first time, it is necessary to identify the indicators of soil quality: the content of heavy metals (Pb, Cd, Cr, Cu, Ni, Zn and Hg), granulometric composition and pH.

3. Results and discussion

In the past, Talkša Lake experienced significant anthropogenic load. Impact of the "Elnias" leather processing plant was especially significant on the composition of trace elements of bottom sediment of the lake. Leather processing industry influenced the increase of concentrations of pollutants such as Cr and Mo in bottom sediment (Taraškevičius and Gregorauskas, 1993). Important influence on the composition of the sediments made urban waste water flowing into the lake. Waste water forms increased Ag, Cr and Zn concentrations (Kadūnas et al., 2001). Previous studies showed that consistently inflows into this lake substantial amount of rainwater from drainage from private houses in the south shore of Lake (Frisk et al., 2004). During this study the highest concentration of heavy metals was found in surface sediments (up to 80 cm thick layer), and followed by their gradual decrease with depth (Fig. 2). Upper sediment layers shall be attributed to 1st category of sludge, which is used for fertilization and pit recultivation all analysed metals concentrations are allowed.

When assessing sapropel in Talkša Lake according to LAND 20-2005 (2005), maximum concentration of Cr ($257.6\text{mg}\cdot\text{kg}^{-1}$) in the upper sapropel layer determined its assignment to the sludge of category II. However, mean concentration of Cr ($76.4\text{mg}\cdot\text{kg}^{-1}$) in the upper layer similarly to concentrations of other explored elements, would be classed as sludge of category I. Vertical section of sapropel in the lake contains horizons which are more polluted with heavy metals, but the concentration of heavy metals within different depths decreases and does not have great effect on the whole sapropel layer. Previous studies (Kadūnas et al., 2001) showed that the sapropel of this lake should be classed as sludge of category III due to the concentrations of Cr that exceeds the maximum allowable level ($\text{Cr} > 400\text{mg}\cdot\text{kg}^{-1}$) by a factor of two. But according to the determined concentrations of Ni, sapropel could be classed to category II. Analysing distribution of chemical elements in vertical sections of sediments other authors divide the bottom sediments into three horizons where different trace elements associations could be distinguished.

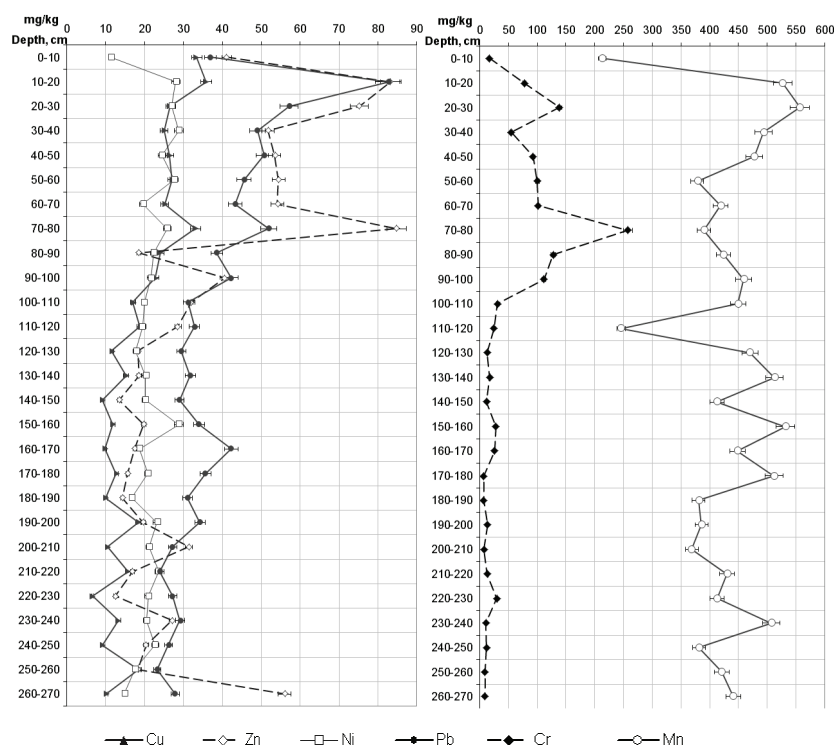


Fig. 2. Distribution of concentrations of heavy metals in the vertical section of sapropel in the northern part of Talkša Lake

First horizon is in the depth from 0 till 0.5 m, second – from 0.5 till 12 m, third – from 12–13 m (Budavičius, 2003). High sorption properties are appropriate characteristics of sapropel; therefore the highest levels of heavy metal concentration in Talkša Lake are recorded in surface layers, whereas the levels of concentration of heavy metals gradually decrease with depth. From 1.1 till 2.1 times higher concentration of Cu, Zn, Cr, Ni, Pb and Mn was determined in the first horizon in comparison with second horizon. Still if sapropel were mixed within all layers, samples recovered from this part of the lake would become a valuable excavation widely used for purposes of economic need. Study results showed that after cleaning the sediment up to 0.5 m in the northern part of lake, and the Cr concentration in the next layer (within 0.5–1 m) would be about $76.4 \text{ mg} \cdot \text{kg}^{-1}$, the resultant concentration of Cr in the mixed sapropel would be about $108.2 \text{ mg} \cdot \text{kg}^{-1}$. Proper sapropel may well be used for growing not only food products (vegetables and fruit trees), but also graminaceous plants for energy production. After proper preparation, the plants may be used to produce heat. In order to guarantee good and fast growth of such plants, it is advisable to fertilize them with sapropel. According to scientists, sapropel is an ecological fertilizer for all agricultural crops (Ciūnys et al., 1998). Agrochemical research on fertilization with sapropel reveals that it is highly effective in increasing and quickening the harvest of vegetation (Ciūnys et al., 1998; Katkevičius et al., 1998).

During the cluster analysis of vertical distribution of heavy metals of sapropel in Talkša Lake, all elements can be divided into two groups

(Fig. 3). The dendrogram clarifies the influence and association of the clusters or groupings by their relative elemental concentrations at each site (Sekabira et al., 2010). The first group is Cu, Ni, Zn, Pb and Cr, and the second – is Mn. The elements of first group are very similar according to their distribution nature in the vertical section of bottom sediment. Elements of this group are biogenic-technogenic (Budavičius, 2003).

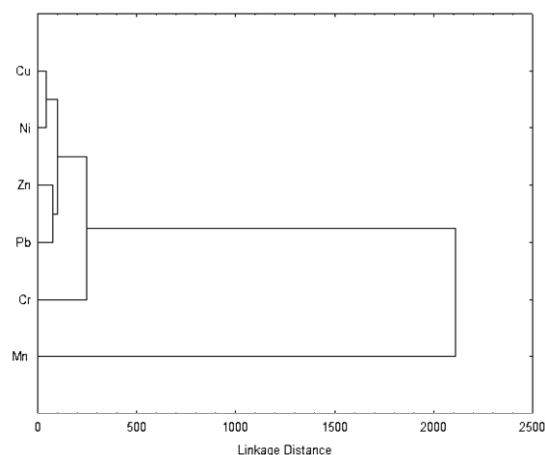


Fig. 3. Cohesion of heavy metals in sapropel of Talkša Lake (within entire vertical section)

The results of cluster analysis showed proper homogeneity of obtained data of Cu, Ni, Zn and Pb. Similar results were obtained Sekabira (2010). Therefore, on the basis of similarity coefficients, Pb, Zn and Cu originated from mixed sources or a retention phenomenon. Distribution and the results of

chromium analysis are ranged in a slightly different order and form a separate section of the first group. Cr content originates from lead processing, when “Elnias” leather processing plant used to operate (Taraškevičius and Gregorauskas, 1993). Formation of levels of chromium in sediments is a specific one in comparison to the distribution of other heavy metals in sediment, which was influenced by trace elements delivered from the city together with air and wastewater pollution.

The amount and distribution of Mn has not been influenced by anthropogenic activity therefore this element forms a separate group. Sekabira (2010) identified, that Mn formed separate cluster and originated from terrigenous source.

Factorial analysis showed the same trends. The first group explains 60.9%, while the second 21% dispersion of data, i.e. both groups explains 82% of the total data dispersion. Some local factors have also been taken into account, such as content of organic matters in sediment, which may affect the accumulation of trace elements and heavy metals in bottom sediments. Organic matter is an important sorption media, especially for metal ions. It can result organometallic compounds, thus affects micronutrient composition of the sediment (Budavičius, 2003). Sapropel can be assigned to different categories, according to the content of organic carbon in it. Lake sediments, where organic carbon content is less than 50% and large amounts of silica are found, is named siliceous sapropel.

Sapropel with content of organic carbon of 70% or more is called organic. High content of organic carbon shows that sapropel can be useful for the soil nutrients that are necessary for the growth and development of plants for the improvement of fertility,

and also can be used for production of biofuel briquettes for heating. The content of organic matter in exploratory bottom sediment of the lake ranged from 26% to 48%, while inorganic – from 1% to 8% (Fig. 4). We have determined lower heavy metals content compared to other places of the lake, where organic matter in the sediment is up to 40% (Kadūnas et al., 2001). The highest concentration (42–48%) of organic carbon was found in the depth of 60–130 cm, while in the deeper layers (150–160 cm) content of organic carbon decreased to 26–29%. However in the depth of 160–270 cm concentration of organic carbon gradual grows up to 40% (Fig. 4).

Trends of pH alternations in vertical section of sediment have been observed. The average pH in test samples was 7.46, while the variation of pH data within the vertical sediment profile was 0.02. This shows a high homogeneity of data (Fig. 4).

Various researches obtained different results during investigations of accumulation of heavy metals in the sapropel of Lake Talkša. Baubinas (2003) determined that Cr concentration in biogenic sediment exceeds the background concentration by 5.7 times and Ni by a factor of 1.6. Keraševičius et al. (2008) indicated that content of Cr and Ni exceeded the background concentrations in biogenic sludge of the lake by 16.8 and 8.2 times, accordingly.

Frisk (2004) reported that highest concentration of Cr were found in the depth from 2.3 to 3.0 m, in the northern part of the lake, and exceeded the background concentrations in biogenic sediments by 13.5 times.

During this investigation sediments were sampled from fragmentarily different places and from different depths. Therefore, the results are very random.

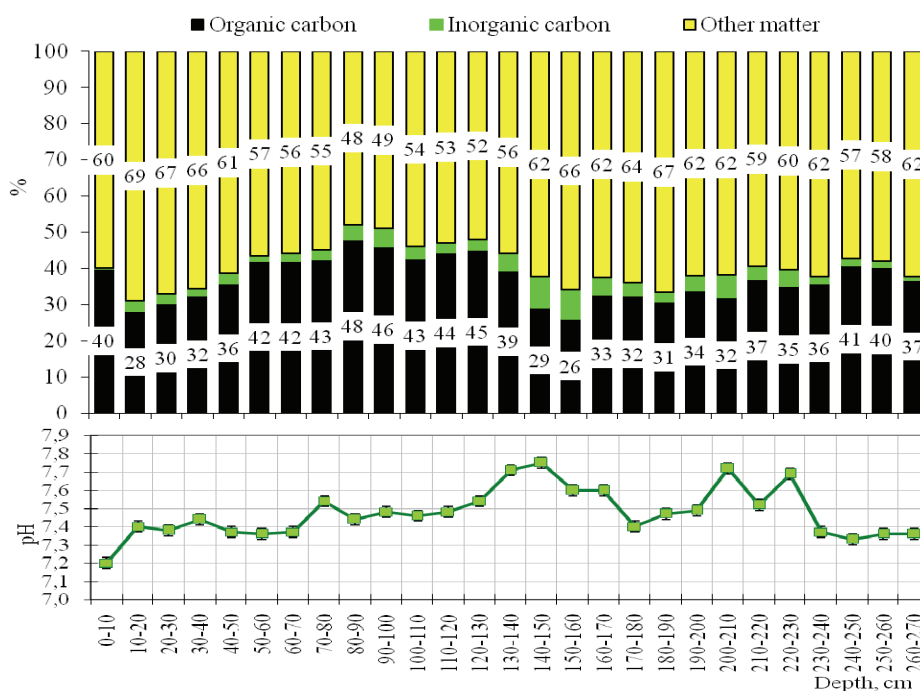


Fig. 4. Distribution of concentrations of organic, inorganic carbon and pH in the vertical section of sapropel in the northern part of Talkša Lake

Ni concentration was not determined during this investigation. Such mismatch of study data could be determined by the choice of different test sites, sampling depths and variations in sampling methods, differences in sample preparation, analytical methods and equipment. However, content of organic matter in the samples also has significant influence. As mentioned above, content of organic matter in analyzed samples was higher, and heavy metals in such sapropel are slightly diluted. It can be argued that the content of heavy metals in samples taken from other places of the lake where organic matter is up to 40% will be higher.

Researches of heavy metal concentration levels in Talkša Lake in Lithuania have revealed that elemental composition of sapropel is different in individual cases and in order to start an expansive use of sapropel it is indispensable to carry out thorough analysis of the composition.

4. Conclusions

Levels of heavy metal concentration in the mixed sapropels of Lake Talkša fell are below the maximum limit values set for contaminated sludge, so that sapropel can be used for soil fertilization and pit recultivation, as provided by the LAND 20-2005 normative. The amount of heavy metals in the sapropels of Lake Talkša meets the requirements for 1st category sludge and it may be used almost without restrictions.

Our results showed higher concentrations by factors of Zn-2.1, Cu-1.8, Cr-1.7, Pb-1.6, Ni-1.1 and Mn-1.1 in the upper layers (0–0.5 m) of lake sediment compared to lower layers (0.5–2.7 m).

The highest concentration of heavy metals was found in surface sediments (up to 80 cm depth), and followed by their gradual decrease with depth. Mixed sapropel from all analysed layers is not polluted with heavy metals and the metal concentrations contained therein can be considered as the content of valuable trace elements. Sapropel recovered from this part of the lake would become valuable material widely used for purposes of economic needs if it is used as a mixture of all of layers. The analyses of sapropel has disclosed that the sapropel from Talkša Lake in Lithuania may extensively be used in agriculture (as biocompost, growth stimulator for vegetation, fertilizer and forage additive), in industry (for diluents, binders in panel production) and in medicine (as curative mud and masks), but it is indispensable to carry out extensive analysis of sapropel before starting to use it.

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OPTIMIZATION OF REDUCTION OF COPPER USING *Stenotrophomonas maltophilia* PD2 BIOMASS AND ARTIFICIAL NEURAL NETWORK MODELING

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Abstract

Copper resistant bacteria, *Stenotrophomonas* species was isolated from a soil from Dhapa, a solid waste disposal site at Kolkata, India. This copper-resistant bacteria *Stenotrophomonas maltophilia* strain PD2 which can reduce copper from aqueous solution, was isolated and reported for the first time. Dead bacterial biomass prepared and used to remove Cu (II) from aqueous solution was investigated using batch techniques. The influence of different parameters on copper uptake by dried biomass, such as initial copper concentration and initial pH of the solution was studied at different intervals of time. A maximum of 83% copper removal efficiency was obtained using 0.5g biomass and 50 mg L⁻¹ copper concentration. Optimization of process parameters was performed using Response Surface Methodology (RSM). The multiple correlation coefficient (R²) was found to be 0.9990. The deviation between theoretical and experimental results was 0.016%. Computational simulated artificial neural network (ANN) was developed to get a good correlation between the input variables responsible for copper removal and the output parameter (% removal) of the process. The correlation coefficient (R) of ANN is 0.958. The optimization procedure of biosorption showed a close interaction between the experimental and simulated values of copper removal.

Key words: Artificial Neural Network (ANN), biosorption, Copper (II) resistant bacteria, optimization, Response Surface Methodology (RSM)

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1. Introduction

As shown in the report of United States Environmental Protection Agency (USEPA, 1978), industrial effluent contains different toxic organic and inorganic components. Heavy metals from industrial effluents (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc) can have toxic effects on human health and environment (Ghosh et al., 2013; Suditu et al., 2013). It is important to mention that heavy metals are not biodegradable and reach the living body via bioaccumulation and biomagnification.

Copper is an essential heavy metal for living organisms, but it can generate some negative impacts in higher concentration (Saha et al., 2008, 2010). Some studies showed that copper can produce risks for human health at levels of 100-500 mg day⁻¹ (Chong and Volesky, 1995; Norton et al., 2004).

Biosorption is an efficient process to remove toxic elements (heavy metals, dyes and etc.) from aqueous solution using biomass (Cetinkaya et al., 1999; Parvathi et al., 2007; Sahan et al., 2010; Wang et al. 2006; Zouboulis et al. 2003). There are two types of biosorption: a) active biosorption, b) passive biosorption. In active biosorption live microorganisms metabolically uptake toxic elements

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whereas in passive biosorption dead biomass of microorganisms used to remove heavy metal from aqueous solution (Ghosh and Saha, 2012).

Yeast, bacteria, fungi, algae etc. are used as biosorbents for heavy metals and different toxic organic elements reduction (Bulgariu et al., 2013; Ghosh et al., 2014; Jaafarzadeh et al., 2014; Sepehr et al., 2014; Tahir and Iram, 2013). The major advantages of biosorption over mainstream treatment process include low cost, high efficiency, minimization of chemical and or biological sludge, and regeneration of biosorbent, recycles of the biosorbent and possibility of metal recovery. Except microorganism cells there are also use of several natural biosorbents such as rice husk, wheat shell, trees bark, leaves, vegetables peels, cereal peel, fruits peels, etc. for removal of heavy metals (Basci et al., 2004; Mesci, 2013; Teixeira Tarley et al., 2004).

The present study aim was to investigate the capacity of copper biosorption using the dead biomass of the isolated novel copper resistant bacteria *Stenotrophomonas maltophilia* strain PD2, isolated from a soil of polluted wasteland (Dhapa, Kolkata, India). The batch study involved changing one independent parameter (pH, copper concentration) while maintaining others at a fixed level.

To optimize the biosorption of copper response surface methodology (RSM) was used. RSM is a statistical technique applied for optimizing the processes parameters and evaluates their interactions (Garg et al., 2009; Jain et al., 2011). Design-Expert 7.0.0 software (Stat Ease, USA) was used for this study. In this study, 2^3 full factorial central composite surface methodology design with 20 experimental runs including 6 replicates was conducted.

Artificial neural network model was employed for designing the biosorption process. A multilayer feed-forward neural network model was applied to predict the copper removal efficiency of the biosorption process by bacterial dead biomass.

2. Materials and methods

2.1. Bacteria isolation and cultivation

Soil was collected from Dhapa, a solid waste disposal site at Kolkata, India. 1 g of soil was diluted to 10 mL sterile normal saline water and serial dilution was followed upto 10^{-7} times. Then nutrient agar plates containing different copper ion concentrations (10 - 250 mg L^{-1}) was inoculated by the soil serial dilution's solution of 10^{-7} . These nutrient agar plates were kept for incubation at $30^\circ C$ for 24 hours. At 200 mg L^{-1} Cu(II) (using $CuSO_4 \cdot 5H_2O$ in nutrient agar plate) maximum copper resistance of the bacteria was found. Nutrient broth and nutrient agar were supplied by Himedia (India). For further use the isolated bacteria were preserved in slanting condition in a copper added nutrient agar test tube in the refrigerator.

2.2. Bacteria characterization

According to the nucleotide homology and phylogenetic analysis the micro-organism was determined to be *Stenotrophomonas maltophilia* strain PD2. The bacterial 16s RNA sequence has been published in the GenBank under the Accession Number: *Stenotrophomonas sp.* (pd2.sqn PD2 JQ809229).

2.3. Preparation of the biosorbent for biosorption

Stenotrophomonas maltophilia was inoculated in conical flasks containing nutrient broth and was kept in an incubator at $30^\circ C$, 110 rpm for 2 days. After incubation, the biomass was harvested from the growth medium and washed thoroughly with distilled normal saline water. After that the dead bacterial biomass was dried at $60^\circ C$ in hot air oven for overnight.

For harvesting the bacterial biomass nutrient broth was used giving a yield of 2 g L^{-1} biomass (approximately).

2.4. Preparation of copper solution

A stock copper solution (1000 mg L^{-1}) was prepared by diluting 3.93 g copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) dissolving in 1 L distilled water. $CuSO_4 \cdot 5H_2O$ was supplied by Merck. Using the stock solution 10 - 100 mg L^{-1} copper solution was prepared for the biosorption study. For pH adjustment $0.1(N)$ HCl and $0.1(N)$ NaOH solution was used and for pH calibration, the pH meter (ELICO) was used.

2.5. Batch biosorption experiments

Cu (II) solutions used in this study were prepared from 1 g L^{-1} stock solutions of Cu (II) obtained by dissolving $CuSO_4 \cdot 5H_2O$ in double distilled water. Batch studies were carried out in 250 ml conical flasks containing 100 mL copper solution in varying copper concentration 10 - 100 mg L^{-1} when pH, rpm of the shaker were kept fixed. In the second group experiments pH was varied from 3 - 6 , when Cu conc./rpm were kept fixed. Dead biomass was added in the copper solution.

Batch biosorption studies were carried out in 250 mL conical flasks containing 100 mL copper solution of different copper concentration 10 - 100 mg L^{-1} when pH, rpm of the shaker were kept at fixed values. In the second group experiments pH was varied from 3 - 6 , when Cu conc./ rpm were kept fixed. Dead bacterial biomass was added in the copper solution.

After biosorption, remaining copper ions in the solution were determined spectrophotometrically at 460 nm (Saha et al., 2010). Sodium diethyl dithiocarbamate (obtained from Loba) was used as complexing agent (Snell and Snell, 1959). Copper

removal percentage by biosorption was obtained by using the formula (Eq. 1).

$$\% \text{Removal} = \left\{ \frac{(C_0 - C_1)}{C_0} \right\} \times 100 \quad (1)$$

The concentrations of Cu were detected using Techcomp UV 2300 Spectrophotometer.

2.6. Optimization experiments

The effect of biosorption parameters namely initial copper concentration, pH of the solution and contact time on percentage removal of copper was studied by statistically designed experiments and optimized by response surface methodology. The percent removal of copper was taken as response of the system. The central composite design (CCD) is standard design which is ideal for series of experiments and allows a reasonable amount of data for testing lack of fit while not requiring an unusually large number of design points. Therefore, CCD with three variables initial Cu(II) concentration: - 15–50 mg L⁻¹, initial pH: - 3.5–5.5 and contact time: - 60–150 minutes was applied using Design-Expert 7.0.0 trial.

The quadratic equation model for predicting the optimal point was expressed according to Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^K \beta_i X_i + \sum_{i=1}^K \beta_{ii} X_i^2 + \sum_{i=1}^K \sum_{j=i+1}^K \beta_{ij} X_i X_j + \epsilon \quad (2)$$

where Y is the predicted response, Xi refers to the coded variables, β_0 , β_i , β_{ii} , β_{ij} are the regression coefficients and ϵ is the statistical error. Three factors were studied and their low and high levels are given in Table 1.

Table 1. Experimental range and levels of independent process variables

Independent Variables	Range and levels(coded)				
	- α	-1	0	+1	+ α
pH(A)	2.81821	3.50	4.50	5.50	6.18179
Copper concentration, mg L ⁻¹ (B)	3.06863	15.00	32.50	50.00	61.9314
Time, min(C)	29.3193	60	105	150	180.681

2.7. ANN Modeling

The fundamentals of artificial neurons are inputs, outputs and mathematical function which decide the activation of the neuron. To process data and validate a model artificial neural networks (ANN) combine artificial neurons. ANN is group of mathematical and computational model which is exalted using the structure and functional expressions of biological neural networks (Lee et al., 1998).

For copper biosorption analysis, an artificial neural network model has been applied successfully. To develop ANN model for biosorption, MATLAB 7 software (The Mathworks, Inc., Ver. 7.0.1) was used. In the present experiment, a three-layer feed forward backpropagation neural network with a linear transfer function was formulated for modeling of copper biosorption using the bacterial biomass. A neural network model's complexity is detected by the number of hidden nodes. Also presence of many neurons in the hidden layer may also induce over fitting of the model (Kumar et al., 2009).

3. Results and discussions

3.1. Batch studies

3.1.1. pH effect

Various factors such as initial pH, initial metal concentration, contact time, temperature and weight of the biomass influence the biosorption of metals on the surface of bacterial biomass. The batch study with different pH was conducted using 0.15 g of biomass in 100 mL Cu solution of concentration 50 mg L⁻¹. At pH 6 maximum Cu(II) removal was found. For precipitation problem of copper salt above pH 6, higher pH range was kept upto 6.

The metal uptake capacity of the bacterial biomass at the corresponding equilibrium conditions was determined using Eq. (3):

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (3)$$

where, q_e is the amount of the metal uptake by the biomass (mg g⁻¹) in the equilibrium; C_0 is initial metal ion concentration in solution (mg L⁻¹); C_e is the equilibrium metal ion concentration in solution (mg L⁻¹); V is volume of the medium (L); and M is the amount of the bacterial biomass used in the reaction mixture (g).

It was observed that as the pH increased, the copper uptake by biomass increased (Fig. 1). Metal uptake was maximum (11.86667 mg g⁻¹) at pH 6, during 180 minutes and using 0.15 g biomass in 100 mL solution.

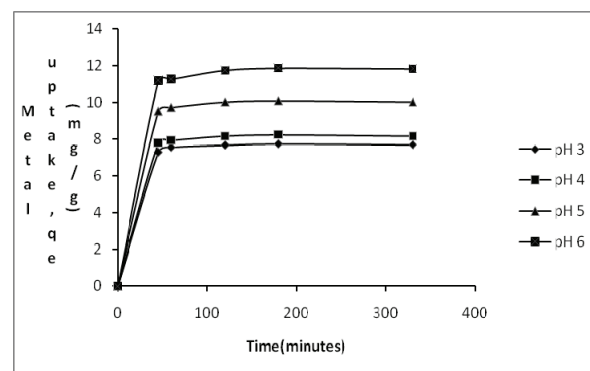


Fig. 1. Metal uptake capacity of biomass at different contact times and different pHs

3.1.2. The effect of initial copper concentration on biosorption

The increase in initial metal concentration resulted in increase in uptake capacity of metal from 10 to 50 mg L⁻¹. The metal uptake was found maximum at 50 mg L⁻¹ copper concentration. The maximum removal found to be 83.8283% at 50 mg L⁻¹, 180 minutes using 0.5 g dead biomass in 100 mL. Fig. 2 shows that a maximum metal uptake by biomass was obtained at 50 mg L⁻¹ Cu(II) concentration.

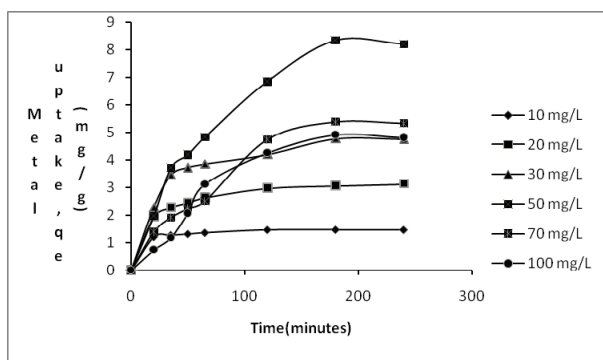


Fig. 2. Metal uptake capacity of biomass at different contact time at different copper concentration

3.1.3. Effect of contact time on biosorption

The effect of contact time (30 min to 240 min) on the biosorption of Cu (II) by dead biomass was studied. The maximum removal of copper was found in 180 minutes when the removal was 83.38% (Fig. 3). Copper concentration was kept fixed at 50 mg L⁻¹, and biomass dosage was 0.5 g/100 mL solution. After 180 minutes, the equilibrium was started.

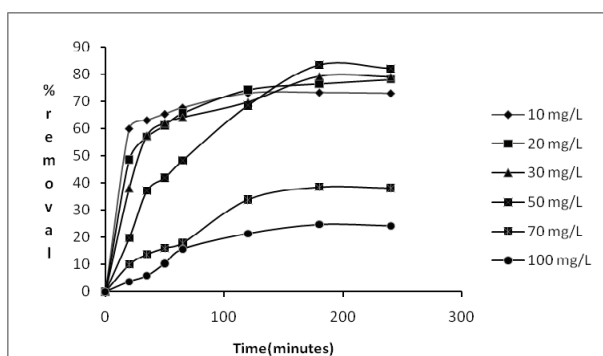


Fig. 3. Removal efficiency of Cu at different time at different copper concentration

3.1.4. SEM analysis of biomass

The scanning electron micrographs were analyzed using S-530, Hitachi Scanning Electron Microscope (Ghosh and Das, 2014).

Scanning electron microscopy analysis was performed to analyze the surface of the bacterial biomass before biosorption (Fig. 4), after biosorption (Fig. 5) and after desorption (Fig. 6). Fig. 4 is very rough in outer surface where Fig. 5 is smooth in surface. The rough surface area of bacterial biomass

(Fig. 4) can help to increase the copper biosorption. Fig. 6 is rougher in surface than Fig. 5.

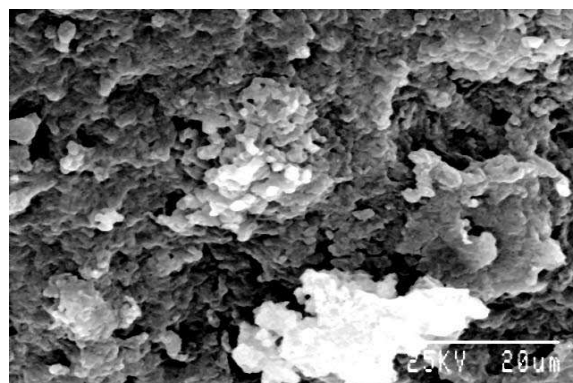


Fig. 4. SEM analysis of the of the bacterial biomass

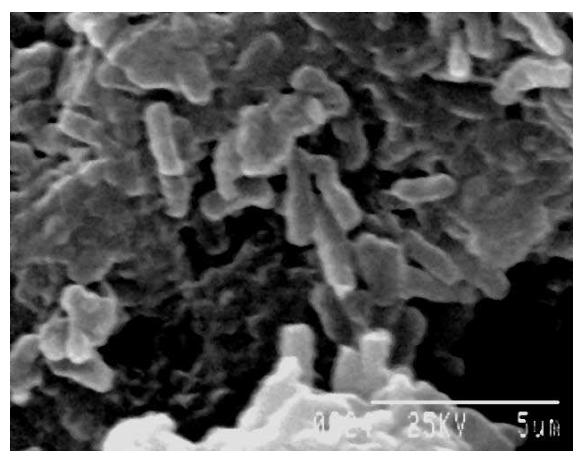


Fig. 5. SEM analysis of the bacterial biomass, after copper biosorption

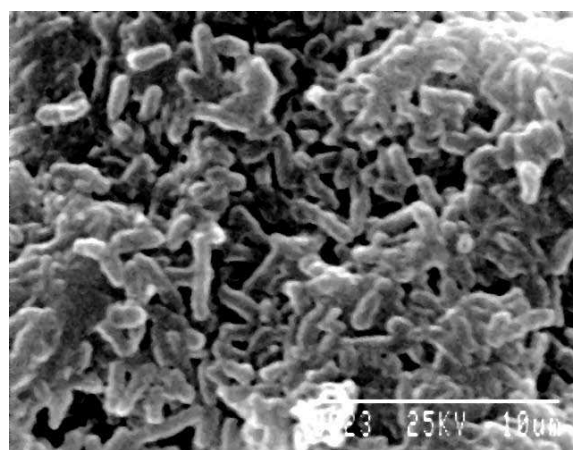


Fig. 6. SEM analysis of biomass of the bacterial biomass, after desorption

3.2. Optimization of passive biosorption

Percentage copper removal was studied using central composite design (CCD). Twenty experiments were performed according to 2³ full factorial central composite design consisting of factorial points (coded to the usual ±1 notation), axial points (±α) and six replicates at the centre

points (0), and each of the experiment was conducted in duplicates.

An empirical relationship (Eq. 4) between the response and the independent variables has been expressed by the following quadratic model. CCD equation of actual factors:

$$R_1 = 55.06932 - 23.59705A - 0.83085B + 0.42324C - 0.035857AB - 0.048444AC + 0.00286667BC + 4.70837A^2 + 0.010248B^2 - 0.000531239C^2 \quad (4)$$

where, A = pH of the solution, B = copper concentration in the solution (mg L^{-1}), C = contact time (minutes).

The equation was confirmed using the statistical ANOVA (analysis-of-variance) analysis, to decide the importance of each term in the equation and to estimate the goodness of fit. Response surface graphs were drawn for the experimental results found from the effect of different variables on the percentage removal of copper in order to determine the individual and cumulative effects of these variables and the mutual interactions between them. The F value (1139.45) with a low probability ($P < 0.0001$) ensures that the model is significant. The multiple correlation coefficient (R^2) also presents the goodness of the model. Moreover, R^2 value is 0.9990 means that more than 99% of the data deviation can be expressed by the developed quadratic model, and the predicted R^2 values are in agreement with adjusted R^2 , which means all the terms showed in the model are significant. In this case, the lack of fit is non significant (more than 0.05) means the quadratic model is effective for the biosorption study (Ghorbani et al., 2009; Hamsaveni et al., 2011).

3.2.1. Effect of initial solution pH and initial copper concentration

The effect of different levels of initial solution of pH and copper concentration on biosorption using

dead bacterial biomass can be predicted from the contour plot as shown in Fig. 7. The contour plot (Fig. 7) showed copper removal percentage increases with increase in pH and initial copper concentration.

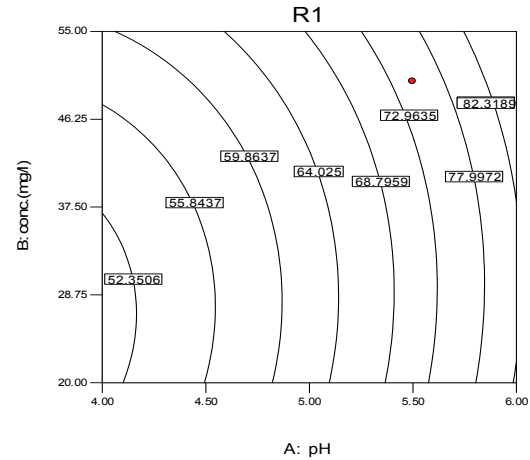


Fig. 7. The contour plot shows the relationship between initial pH and initial copper concentration with the R1

3.2.2. Effect of initial solution pH and contact time

Percentage removal gets increased with increase in pH and time. At pH 5.50, contact time 150 minutes the optimum removal was obtained 74.9978%, when copper concentration was fixed at 50 mg L^{-1} . From the contour plot (Fig. 8), it was observed that copper removal percentage increased with increase in pH and contact time.

3.2.3. Effect of initial copper concentration and contact time

Percentage removal gets increased with increase in initial copper concentration and time. At 50 mg L^{-1} copper concentration and contact time 150 minutes the optimum removal was obtained 74.9978%, when pH was fixed at 5.50. The contour plot (Fig. 9) showed copper removal percentage increases with increase in copper concentration and contact time.

Table 2. Regression analysis by using central composite design

Model Term	Coefficient estimate	Standard error	F value	P value
A	12.53	0.16	5999.33	<0.0001
B	-0.44	0.16	7.35	0.0219
C	8.41	0.16	2702.97	<0.0001
AB	-0.63	0.21	8.82	0.0141
AC	-2.18	0.21	106.44	<0.0001
BC	2.26	0.21	114.14	<0.0001
A ²	4.71	0.16	894.44	<0.0001
B ²	3.14	0.16	397.45	<0.0001
C ²	-1.08	0.16	46.69	<0.0001

Table 3. Analysis of variance for the response surface quadratic model for copper removal

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	Probability>F
Model	3662.95	9	406.99	1139.45	<0.0001
Residual	3.57	10	0.36		
Lack of fit	2.41	5	0.48	2.08	0.2199
Pure error	1.16	5	0.23		
Total	3666.53	19			

$R^2 = 0.9990$; adjusted $R^2 = 0.9981$; predicted $R^2 = 0.9945$.

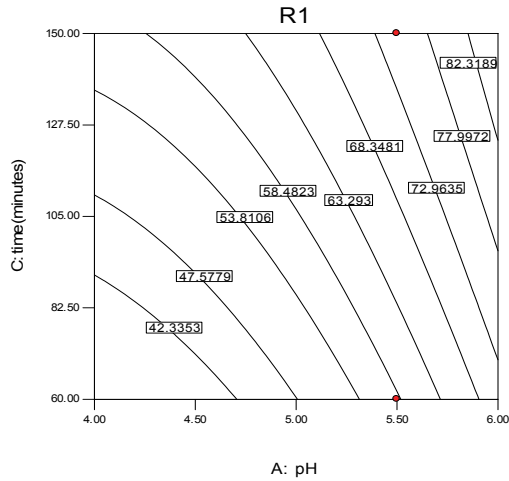


Fig. 8. The contour plot shows the relationship between initial pH and contact time with the R1

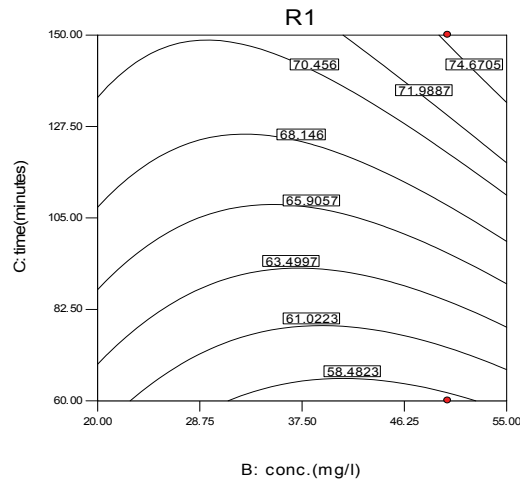


Fig. 9. The contour plot shows the relationship between initial copper concentration and contact time with the R1

3.2.4. Optimization using the desirability functions

A minimum and a maximum level must be provided for each variables included in the study. Starting from representing points in the design improves the chances for finding the ‘best’ local maximum (Amini et al., 2008; 2009). The numerical optimization was used to find a point that maximizes the desirability function. Level of initial solution pH (3.5-5.5), copper concentration (15-50 mg L⁻¹) and contact time (60-150 minutes) were in between the

range and maximum percentage removal of copper (74.9978%) were set for maximum desirability. Fig. 10 showed a ramp of desirability that was generated from 6 optimum points via numerical optimization.

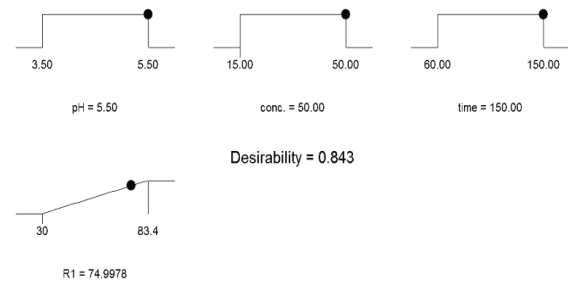


Fig. 10. Desirability ramp for optimization of three goals, namely initial solution pH, copper concentration and contact time of maximum removal of copper (R1)

3.3. Artificial neural network training

After testing, it was found that 10 neurons generate minimum error of the training and validation sets. To develop and validate the optimization model of biosorption ANNs were used. The output variable was the percentage copper removal. The network which yielded a coefficient of correlation (R) 0.958 which is near to 1 believed to be an accurate model and was hence selected. The feed-forward networks are bulk of ANN architectures and are mostly tested from the input data using error backpropagation algorithm.

Linear positive transfer function ‘POSLIN’ was picked out as input and purely linear transfer function ‘PURELIN’ was picked out as output to hidden layer mapping. The values of correlation coefficient (R) were determined between 10 repeated run. Fig. 11 shows the regression plot of the trained network. A correlation coefficient of 0.958 was found from the trained network. The high correlation coefficient entailed the significance of the neural model with the experimental data. Table 4 showed that the ‘Levenberg-Marquardt backpropagation (Trainlm)’ algorithm with ‘poslin’ transfer function gave a most reliable result (Sinha et al., 2012).

Fig. 12 showed the comparison of experimental, RSM and ANN results. It was observed that the deviation in both the cases were very low. The deviation was less than 1.4%.

Table 4. The algorithm used in the ANN study

Algorithm for hidden layer	Function for output layer	Transfer function	Transfer function	Correlation efficient (R)
Levenberg-Marquardt backpropagation	Trainlm	Poslin	Purelin	0.958
Resident backpropagation	Trainrp	Poslin	Purelin	0.941
Scaled conjugate gradient backpropagation	Trainscg	Poslin	Purelin	0.934
Conjugate gradient backpropagation with Polak-Ribiere updates	Traincgp	Poslin	Purelin	0.931
Gradient descent with momentum and adaptive learning rate backpropagation	Traindgn	Poslin	Purelin	0.929

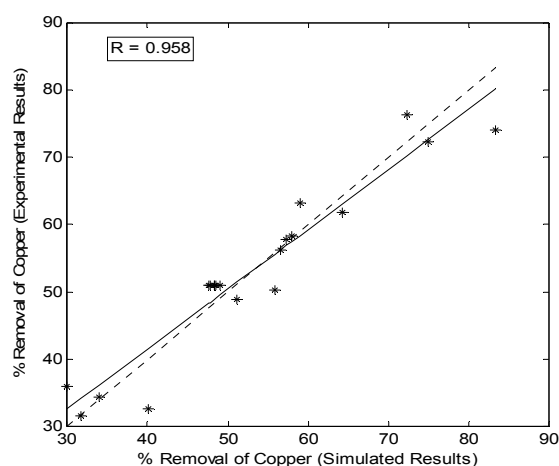


Fig. 11. The regression plot (Simulated vs. experimental results)

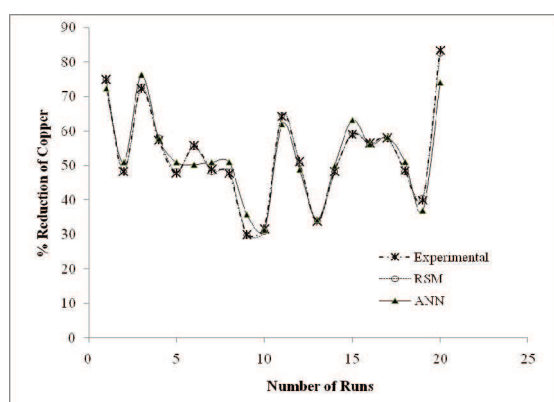


Fig. 12. Experimental results vs. simulated result by RSM and ANN

4. Conclusions

The biosorption of Cu(II) ions were examined using the dead bacterial biomass of *Stenotrophomonas maltophilia* strain PD2. The effect of pH, copper concentration, and contact time on the biosorption was studied. Every process parameters showed strong influences on the biosorption process. An effective removal (74%-83%) was found in the batch and optimization study.

The results concluded that the bacterial biomass may be used as an inexpensive, effective and easily cultivable biosorbent for the removal of Cu(II) ions from aqueous solutions.

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CHARACTERIZATION OF FIRST FLUSH IN URBAN HIGHWAY RUNOFFS

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Abstract

Samples were collected for six months (nine storm events) to observe the contaminant loads from three highway segments at Rawalpindi, Pakistan. The contaminants analyzed include total suspended solids (TSS), total dissolved solids (TDS), total nitrogen (TN), chemical oxygen demand (COD), total organic carbon (TOC), total phosphorous (TP), sulphate (SO_4), chloride (Cl^-), iron (Fe), copper (Cu), zinc (Zn), lead (Pb), and chromium (Cr). Mass vs. volume $[M(V)]$ curves were drawn to investigate and calculate the extent of first flush at the sites selected. The results showed that the contaminant loads at 25% (FF_{25}) and 30% (FF_{30}) of initial runoff volume to be 40 and 44% of the contaminants on average, respectively. Hence, proving the existence of first flush, but questioning the previous definitions. TSS and COD were found to be the dominating parameters in the first flush quality, whereas among the heavy metals Fe and Cr were observed higher. The study not only endorse the existence of first flush but also revealed first flush, to be an unavoidable component of stormwater management, as it had the elevated values of contaminant load.

Key words: event mean concentrations (EMCs), first flush, first flush coefficient, highway runoff quality

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1. Introduction

The large impervious area created by urbanization leads to huge runoff volumes at the drainage point (Lee et al., 2002; Shuster et al., 2005). These high volumes carry high amounts of contaminant concentrations which result from the nonpoint sources and deteriorate the receiving waters (Paul and Meyer, 2001; Robson et al., 2006).

The major components of pollution are TSS, TDS, particulates, and heavy metals, which accumulate during the dry days (Fan, 2014). First flush analysis is the best management tool used to manage these contaminant add-ups through such huge runoff volumes.

First flush is the initial stormwater flow which contains the higher concentration of contaminants (Bach et al., 2010; Bertrand-Krajewsky et al., 1997; Charbeneau and Barrett, 1998; Iqbal and Baig, 2011;

Larsen et al., 1998; Thornton and Saul, 1987). Hence, characterization of first flush is necessary for an efficient stormwater management plan.

First flush effect is “the higher contaminant concentrations washed off by the initial stormwater volume”. It remained a general observation for centuries, but in 70s, the concept was first taken into the discussion of scientist community. For the next many years, first half-inch of the storm was attributed as first flush, commonly known as “the half-inch rule”. This thumb rule is still under observation of a few scientists (Flint and Davis, 2007).

Afterwards, the scientists analyzed first flush chiefly as a function of time and volume. The general definition of first flush was given by Geiger (1987), but the better definition, based on the volume (in terms of time), was proposed by Wanielista and Buchberger (1993); according to which “the first flush occurs if the first 25% of storm runoff (FF_{25})

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transports 50% of the total contaminants washed off'. Similarly, definition tossed by Bertrand-Krajewsky et al., 1997 marked 80% of the contaminants transported in first 30% of the stormwater flow (FF_{30}), which seemed to be very strict. All of these definitions clears that the first flush is a site specific behavior and it has to be checked for all the sites.

Highways are one of the major components of an urban area that contribute high contaminant loads (Iqbal and Baig, 2010; Maltby et al., 1995). Generally, the factors affecting the first flush includes antecedent dry weather period (ADWP) (Li et al., 2007; Schriewer et al., 2008; Yufen et al., 2008), annual average daily traffic (AADT), (Kayhanian et al., 2003), storm intensity and depth (Huang et al., 2007), and amount of contaminants present on the highways (Dumitrescu et al., 2014).

These characteristics are site and event specific, which makes the first flush analysis more critical. In the current study, three highway sections were selected on the basis of traffic count and the catchment characteristics. The contaminants analyzed include total suspended solids (TSS), total dissolved solids (TDS), total nitrogen (TN), chemical oxygen demand (COD), total organic carbon (TOC), pH, electrical conductivity (EC), total phosphorous (TP), sulphate (SO_4), and chloride (Cl^-) and among heavy metals iron (Fe), copper (Cu), zinc (Zn), lead (Pb), and chromium (Cr). The correlation analysis was done for the first flush coefficient and the catchment characteristics. The major objectives of the study were to characterize the highway stormwater runoff in Rawalpindi and investigate the extent of first flush on the basis of volume and time.

2. Materials and methods

We selected three highway segments in the city of Rawalpindi, Pakistan. These sites were located close to each other, which minimized the variability of storm distribution. The proximity of sites also helped in storm intensity calculation, with intensity prediction models, in case of any rain gauge failure. Each site had higher slope, which minimized the time of concentration (the time needed by rain drop fallen at the farthest end of the catchment area to reach at the drainage point) of the storm for each highway segment.

The characteristics of each sampling site are shown in Table 1. If we divide highway segments, on the basis of annual average daily traffic, in three categories; small (< 25,000), moderate (25,000-50,000), and large (> 50,000). S-II and S-III can be termed as large and S-I as moderate trafficked segments. S-I has the lowest area among the other sites observed, though with the highest slope.

On the other hand, S-III had largest area of all the sites with slope of 3%. S-II was intermediate for both area and slope. Landuse for the highway side is also described in the Table 1.

In order to analyze the characteristics of stormwater, the samples were collected manually (Kayhanian and Stenstrom, 2008). Since, the characteristics of stormwater changes with the time and the rain intensity (ultimately the flow), the sampling was done on the basis of time as well as volume. Sampling was done at every 10 min interval, during the storm event, at the discharge point and before getting into the sewer system. Polyethylene bottles (300 and 500 ml) were used for sampling and before use all the containers were acid rinsed. The sample containers were labeled and tightly sealed, immediately after collection.

Table 1. Characteristics of all sampling sites

Site	Area (m^2)	General characteristics	Slope (%)	Traffic
S-I	5300	Highway side commercial market	5	Moderate
S-II	6900	Five star hotel near by	2.4	Large
S-III	41500	No/negligible commercial activities near the highway	3	Large

Total Dissolved Solids (TDS), EC and pH (sensION+ MM150 Portable pH/ORP/EC Multi-Meter) were measured in the field and the samples were transported to the laboratory for further physical and chemical analyses.

The collected samples were analyzed for SO_4 , TP (Spectronic Genesys 5, spectrophotometer), TSS (Gravimetric method, Standard Method, 2005), Cl^- (Argentometry, Standard Method, 2005), TOC and TN (Analytik-jena, TOC analyzer multi N/C UV HS, detection limit; $2\mu g/l$) in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

The heavy metals were analyzed with the help of Atomic Absorption Spectrophotometer (Hitachi Z-8000 Japan) with detection limits for $Cu = 0.3\mu g/L$, $Fe = 0.1\mu g/L$, $Cr = 0.01\mu g/L$, $Pb = 0.03\mu g/L$ and $Zn = 0.01\mu g/L$.

The dimensionless cumulative contaminant load was plotted against dimensionless flow volume at x-axis for the first flush analysis.

The diagonal line was drawn to differentiate the volume-based contaminant mass curve (Bertrand-Krajewsky et al., 1997).

For theoretical calculations of first flush, the $M(V)$ curves were fitted by a power function i.e. the coefficient of first flush "b" value (Saget et al., 1996). Mathematically (Eqs. 1 and 2):

$$F(X) = X^b \quad (1)$$

$$\ln(F(X)) = b \ln(X) \quad (2)$$

where: b = coefficient of first flush; X = cumulative volume / total volume; F(X) = cumulative mass / total mass.

3. Results and discussion

A total of nine storm events were recorded at the rain gauges during the research period and the sampling was done for all the events. The basic storm event characteristics are represented in Table 2, which shows that the rainfall depth was recorded from 4 to 60 mm. Event 8 had the longest storm durations of 175 minutes. The most intense storm event among all was event 2. Antecedent dry weather period between the storm events remained 10 to 31 days.

The pollutograph analysis showed that the peaks of contaminants were followed by the flow peak, which depicted the occurrence of first flush, as discussed by Lee and Bang (2000), while characterizing urban runoff. The pollutograph analysis does not show complete picture of the contaminant behavior during storm events, as it can only depict the general trend of contaminant load in the urban stormwater runoff.

Table 2. Characteristics of the storm events

Event	Rainfall Depth (mm)	Duration (min)	ADWP (days)	No. of samples collected
1	8	40-50	-	4
2	60	70-90	10	8
3	18	60-70	31	6
4	13	30-45	16	3
5	4	30-40	24	3
6	8	60-70	26	6
7	14	100-115	25	11
8	29	170-175	11	17
9	15	95-120	15	10

The M (V) curves were drawn for all the parameters, each depicting a distinctive behavior. Total suspended solids completely showed first flush at S-I and S-II ($b = 0.79$ to 0.86), whereas at S-III TSS was found to be on or just above the diagonal line (slope = 1), representing a slight first flush effect ($b = 0.94$ - 0.98). TP and SO_4 initially did not show first flush at S-I and S-III, but after 20-30% of the volume, the graph fell above the 45° line.

Furthermore, EC and TDS initially showed the first flush, while after 40 to 60% of the flow volume, it was diluted. Similar behavior was shown by TDS, especially at S-III. TOC and TN represented first flush effect in the beginning of the flow, but soon after, it became nearly constant or diluted. Chloride depicted the characteristic phenomenon of the first flush ($b = 0.76$ to 0.88). On the other hand, pH remained almost constant or there was a little change from start to the end of a storm event. The pH ranged from 6 to 7.5, mostly in the acidic range due to SO_4 and NO_3 (Hu et al., 2003).

Heavy metals, released from vehicles with particulate behavior, depicted an excellent first flush at almost all the sites. Among these metals, Cr showed the first flush in almost all the storm events at all the sites. Similarly, Cu represented a pronounced first flush effect, especially at S-II,

satisfying the Bertrand-Krajewski et al. (1998) definition. Zn showed a strong first flush particularly at S-III and S-I. Almost 60 to 85% of Zn was washed away in 30% of the flow in few storms. Compatively, Pb exhibited a moderate first flush effect, but at S-I Pb was washed off upto 75% in 30% of the cumulative volume in one of the storm events. Fe perfectly fell into the definition of Bertrand-Krajewski et al. (1998) in few of the storms at S-II and S-I sampling sites.

Here we only discuss COD, as it serves as a representative parameter for stormwater quality (Lee and Bang, 2000). The M (V) curves for COD at S-I (smallest catchment area) and S-III (largest catchment area) are shown in Figs. 1 and 2. The figures show that COD followed the typical first flush behavior on both the segments. The first flush phenomenon in a few of the storms was not evident at S-III i.e. the first flush effect for COD at S-III was delayed.

The numerical values (b values) of COD M (V) curves are shown as a line graph in Fig. 3. The straight line is drawn at 1 to differentiate the extent of deviation for "b" value against the storm events. The figure represents that the general trend of COD at all highway sampling sites is same, but the extent of the trend is variable. At Event 4, the coefficient of first flush fluctuated drastically at all the sites, which is because of the lesser intensity and duration of the storm event (Gupta and Saul, 1996). At S-I, "b" value is almost in the region of first flush, which is probably because of the higher slope gradient as compared to the other sites. At S-I, the first flush was not shown in Event 9, because of the repair and maintenance activity at the highway during time of study. On the other hand, S-III does not show an effective first flush in larger and intense storm events, but pronounced first flush was observed in lesser duration and intensity events, which is due to a larger drainage area; since, the larger area directly affects the first flush characteristics of the drainage basin (Kang et al., 2006).

On the basis of average "b" values, the relative strength of first flush contaminants remained $Pb > Cr > Cl^- > Fe > SO_4 > Cu > TSS > TDS > TOC > TP > COD > Zn$ at S-I, $Fe > Cl^- > TN > Cu > TSS > Pb > Cr > Zn > TOC > COD > TP$ at S-II, and $TSS > Zn > Fe > Pb > SO_4 > Cl^- > TOC > COD > Cr > EC > TP > TDS$ at S-III. The relative strength depicts that the heavy metals are prone to first flush phenomenon compared to the other parameters. In Table 3, Pearson correlation coefficients of 'b' values against the site characteristics. The table shows that COD, TOC, EC, and TDS are negatively correlated to the catchment characteristics whereas TSS and the heavy metals significantly positive correlated. Therefore, it can be drawn that the particulate parameters are directly influenced by the highway characteristics. The area and Annual Average Daily Traffic are major highway traits that affect the first flush of majority of the parameters. The FF_{25} and FF_{30} were calculated for better description of the first

flush and it was observed that values of both FF_{25} and FF_{30} remained maximum at S-II and minimum at S-III. The average FF_{25} and FF_{30} for all the highway sampling site was 40% and 44%, respectively. Both FF_{25} and FF_{30} were observed maximum at S-II and minimum at S-III. The definition of first flush proposed by Wanielista and Yousef (1993) remained satisfied by the dataset. The results indicated that 33% storm showed compliance with their definition,

whereas only 3% fell in definition by the Bertrand-Krajewsky et al. (1997) definition. The definition of first flush by Barco et al. (2008) is also suitable, which states that 40% of the contaminants were observed in 20% of the flow, but their definition is for the combined sewer. Therefore, there are extensive requirements for redefining the first flush phenomenon, as few of the scientists are trying (Bach et al., 2010; Ma et al., 2011).

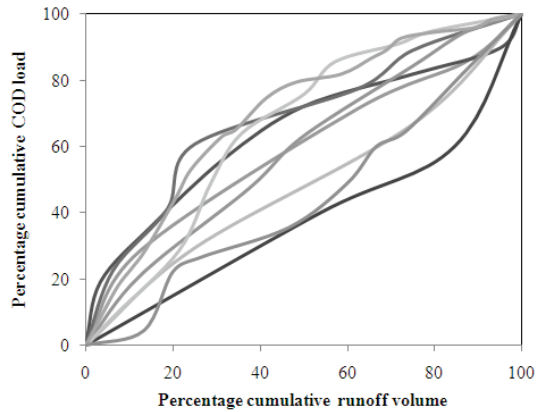


Fig. 1. M (V) curves for chemical oxygen demand at S-I

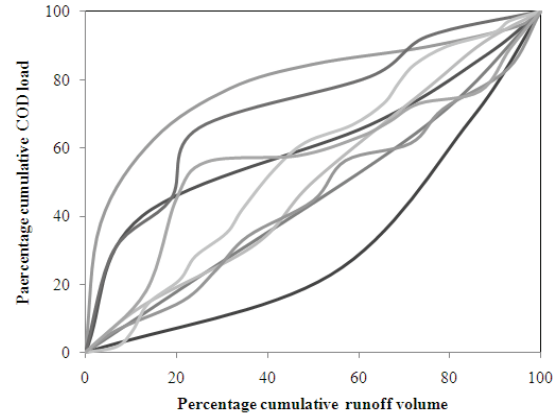


Fig. 2. M (V) curves for chemical oxygen demand at S-III

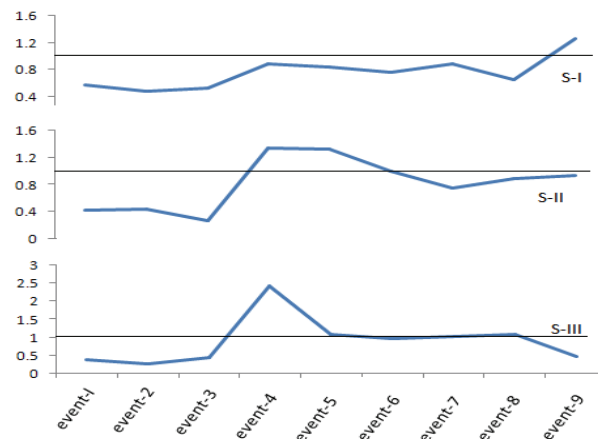


Fig. 3. Coefficient of first flush for chemical oxygen demand at highway sampling sites

Table 3. Pearson correlation coefficient of 'b' values for highway characteristics in Event 2

Parameters	Area	Slope	AADT
COD (mg/L)	-0.85	-0.75	-0.79
TP (mg/L)	-0.12	-0.90	0.34
TSS (mg/L)	1.00	0.78	0.89
SO ₄ (mg/L)	-0.39	-0.74	0.06
Cl ⁻ (mg/L)	0.98	-0.12	0.77
EC (mS/cm)	-0.46	-0.68	-0.02
TDS (mg/L)	-0.26	-0.82	-0.20
TOC (mg/L)	-0.66	-0.49	-0.26
TN (mg/L)	0.46	0.68	0.02
Pb (mg/L)	0.52	0.98	0.85
Cr (mg/L)	0.67	0.93	0.93
Cu (mg/L)	0.94	0.02	0.68
Zn (mg/L)	-0.96	-0.57	-0.98
Fe (mg/L)	0.71	0.43	0.32

4. Conclusions

Urbanization has affected the natural water cycles and hence contributed to floods on one hand and high contaminant loads, on the other. Highways are the major components of urban development, which contribute to higher contaminant loads to the receiving water bodies. On the basis of results we conclude that the first flush is an unavoidable component of stormwater management. It can be used as an efficient stormwater management tool, but there is a need for “storm” characteristics based approach to redefine it. Following are the major conclusions drawn from the study.

- The runoff quality is highly polluted in the city of Rawalpindi, Pakistan especially in terms of TSS and COD.
- The relative strength of first flush contaminants for the highways was found to be $Pb > Fe > TSS > Cl^- > Cr > TN > TOC > Cu > Zn > TP > COD > SO_4 > EC$.
- The highway characteristics significantly affect the first flush behavior of the particulates.
- At all the sampling sites, first flush was comparable to the past definitions, as the coefficient of first flush (b value) remained 0.8 to 1.
- First flush as a function of runoff volume in unit time that initial 30% of the runoff volume (FF_{30}) of stormwater runoff contains 40-50 % of the total contaminants washed off in the storm event.
- First flush is a site specific phenomenon therefore it cannot be defined precisely.

It is recommended that the social, environmental, and seasonal variations may also be monitored in evaluating the first flush; it can answer many questions regarding the contaminant loads. Secondly, the higher values of contaminant load in stormwater runoff needs to be checked before discharging into the streams. Therefore, there should be a legal framework for the stormwater discharges of newly-urbanized developments. Lastly, Pakistan Environment Protection Agency (Pak-EPA) should develop and maintain standards for the stormwater discharges.

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EXAMINATION OF THE USE OF AMMONIUM ACETATE AS LIXIVIANT IN RECOVERY OF ZINC FROM WASTE BATTERIES AND KINETIC ANALYSIS

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Abstract

This study is focused on the dissolution kinetics of zinc oxide in ammonium acetate solutions to recover the zinc from alkaline and zinc-carbon spent battery powders. This study represents a first step for further studies in which actual waste powder is to be used. Therefore, the experiments were performed by using pure zinc oxide powder to evaluate the dissolution behavior of zinc. The effects of ammonium acetate concentration, reaction temperature, stirring speed and solid to liquid ratio on the dissolution of zinc oxide were examined, and a kinetic analysis was performed by using the heterogeneous and homogeneous reaction models. It was determined that the dissolution rate increased with increasing ammonium acetate concentration and reaction temperature, and with decreasing solid to liquid ratio. It was found that zinc oxide was dissolved approximately 99.5 % under the experimental conditions at 1 M, 40°C, 400 rpm, 1/250 g/mL, and 15 min. The kinetic analysis results showed that the dissolution rate fit to the first-order pseudo-homogeneous reaction model. The activation energy of the dissolution process was calculated to be 43.83 kJ/mol. According to the results of this study, ammonium acetate can be used as an effective leach reagent to extract the zinc from spent battery powder.

Key words: battery, dissolution, kinetics, zinc

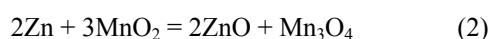
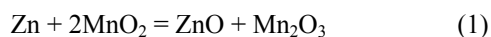
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1. Introduction

Among the nonferrous metals, zinc is the third most used metal after aluminum and copper. Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. Zinc is used in many branches of industry, including galvanizing of steel surfaces, brass and other alloys, dry batteries, paint, fertilizer, and chemicals, etc. It is primarily found in various forms around the world, and is mainly recovered from sulphide concentrates (Jha et al., 2001; Sahu et al., 2004). As a result of the increase in demand for zinc and the gradual depletion of high-grade sulfide ores, numerous researches aimed at recovering of zinc from the oxide and silicate ores, secondary sources and various wastes have been performed (Baba et al., 2009; Kunicky et al., 2008; Safari et al., 2009). Zinc

can be found in the form of metal, oxide or alloy in the secondary sources (Kunicky et al., 2008).

The zinc-carbon and alkaline zinc-manganese batteries are widely used because of the versatility, low maintenance, and favorable electrical properties/price ratio. The zinc-carbon and alkaline zinc-manganese batteries contain mainly zinc, manganese dioxide and electrolyte (e.g., ammonium chloride, potassium hydroxide). The oxidation and reduction reactions occur during discharge of a battery. The simplified overall battery reactions for the zinc-carbon and alkaline zinc-manganese batteries can be written as below (Eqs. 1 and 2) (De Souza et al., 2001; Gega and Walkowiak, 2011).



The resulting waste-battery powders after using the batteries contain significant amounts of Zn, ZnO, MnO₂, Mn₂O₃ and Mn₃O₄ depending on the discharging reactions. Hence, they can be accepted as secondary sources for the production of zinc and manganese. Moreover, recycling of the major components of spent batteries also can be considered to be a beneficial way to prevent environmental pollution and decrease raw material consumption (e.g., zinc and manganese ores) (De Souza et al., 2001; Gega and Walkowiak, 2011; Jaapar and Ahmad, 2006).

Pyrometallurgical and hydrometallurgical methods can be employed for processing of waste batteries. The hydrometallurgy is a more environmentally friendly and economical process to evaluate the waste batteries. The first step of the hydrometallurgical processing is the leaching of solid material by an acidic or a basic solution. Afterwards, the leach solutions are subjected to separation and purification processes, like precipitation, solvent extraction, adsorption, and ion-exchange. Ultimately, a metal or its compound is produced by applying chemical or electrochemical methods (Venkatachalam, 1998).

Recovering of zinc from spent batteries has been investigated by using different lixiviants by means of hydrometallurgical methods. Sulfuric acid solutions have been generally used for the zinc recovery from waste batteries (De Souza et al., 2001; Ferella et al., 2010; Gega and Walkowiak, 2011; Haghshenas et al., 2007; Pedrosa et al., 2009). Hydrochloric acid (Baba et al., 2009), ammonia (Senanayake et al., 2010), and sodium hydroxide solutions (Shin et al., 2009) have been employed for the leaching of waste-battery powder. The solutions containing both inorganic and organic acids have been performed for the hydrometallurgical processing of spent batteries (El Nadi et al., 2007; Ferella et al., 2006; Sayilgan et al., 2010).

Because the kinetic information is required for the efficient design of a hydrometallurgical plant, examination of the kinetic of leaching reactions is important (Crundwell, 1995). In the recovery studies of metals from waste batteries, it has been generally focused on the effect of the leaching parameters, and there is very little information about the leaching kinetics. Knowledge of the dissolution kinetics of metallic values in various wastes is important to evaluate their leaching behaviors. The major components in spent battery powders are zinc and manganese compounds. The separately determination of the solubility behavior of zinc and manganese can provide an advantage for selection of solvent to be used in the leaching process. If these metals are dissolved simultaneously, then it needs to perform the additional processing steps to separate them. Manganese (IV) oxide is partly soluble in strongly acidic medium. Hence, the use of less acidic or basic lixiviants than strong acids may be more suitable for the leaching of waste-battery powder. In this case,

manganese does not leach while zinc passes into the solution by dissolving from the solid matrix. Zinc can be easily recovered in the form of metal or compound from such a solution. Ammonium acetate is a neutral salt and can be used as leach reagent in the dissolution processes. This study represents a first step for further studies in which actual waste powder is to be used. The dissolution experiments were carried out by using pure zinc oxide powder. The effects of the solution concentration, solid to liquid ratio, stirring speed, and reaction temperature on the dissolution of zinc oxide were determined, and a kinetic analysis was performed by using the heterogeneous and homogeneous reaction models.

2. Experimental

The dissolution experiments were carried out in a 500 mL jacketed glass reactor equipped with a temperature control unit, a mechanical stirrer, and a condenser to avoid of solution by evaporation. The mechanical stirrer had a digital controller unit, and its agitator shaft and blade (45 mm-diameters) was made of Teflon. Temperature control unit had a constant-temperature-circulator.

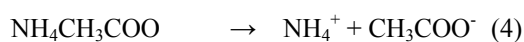
The experimental procedure was initiated by adding 250 mL of an ammonium acetate (98%, Sigma) solution into the glass reactor and bringing it to the desired reaction temperature. A given amount of zinc oxide (99%, Sigma) was then added to the solution, and the reactor content was stirred at predetermined stirring speed. The progress of the reaction was followed by determining the dissolved zinc in the solution. Aliquots of 2 mL were withdrawn at regular intervals during the reaction, and these were immediately filtered. The dissolved zinc were determined complexometrically using Titriplex III (99.5%, Merck) solution as titrant and buffer tablet (contain Eriochrome Black T) (Merck) as indicator (Gülensoy, 1984). The conversion fraction of zinc was calculated as follows (Eq. 3):

$$x = \text{amount of zinc passing to the solution} / \text{amount of zinc in zinc oxide} \quad (3)$$

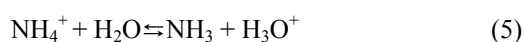
3. Results and discussion

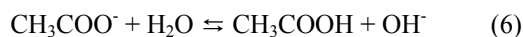
3.1. Dissolution reactions

Ammonium acetate is the salt of a weak acid (acetic acid) and a weak base (ammonia), and has a neutral character. According to the following reaction, ammonium acetate ionizes in aqueous medium (Eq. 4).

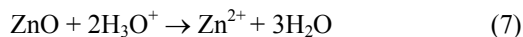


Ammonium and acetate ions both undergo hydrolysis, as shown in the following equations (Eqs. 5 and 6).

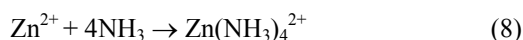




Essentially, H_3O^+ ions are used to dissolve the zinc oxide. Thus, when zinc oxide is added into ammonium acetate solution, the reaction occurring during the dissolution process is likely as follows (Eq. 7):



In addition, the zinc-amine complex may form in the reaction media (Eq. 8).



3.2. Effects of parameters

In the dissolution studies, variables such as reaction temperature, solution concentration, solid to liquid ratio, particle size, and stirring speed are generally chosen as the experimental parameters. The dissolution data obtained are plotted as a function of conversion fraction, and the kinetic analysis is performed. In the present study, the dissolution rate of zinc oxide was determined as a function of time by changing the ammonium acetate concentration, solid to liquid ratio, stirring speed, and reaction temperature. Before studying the effects of other parameters that may influence the dissolution rate, the effect of stirring speed was firstly examined. The experiments were carried out at stirring speeds of 200, 300, 400, and 500 rpm to observe the effect of the stirring speed on the dissolution rate.

In these experiments, ammonium acetate concentration, solid to liquid ratio, and reaction temperature were fixed at 0.75 M, 1.0/250 g/mL, and 40°C, respectively. In the stirring speed experiments, it was observed that the particles were fully suspended in the solution at 400 rpm. Below this stirring speed, it was seen that the zinc oxide particles accumulated at the bottom of the reactor. At the stirring speeds above 400 rpm, the experimental results showed that the effect of agitation speed on the dissolution rate can be practically neglected. For this reason, all subsequent experiments were performed at a stirring speed of 400 rpm.

To investigate the effect of solution concentration on the dissolution of zinc, the experiments were performed in the range of 0.25 - 1.00 M of ammonium acetate. The reaction temperature, solid to liquid ratio, and stirring speed were kept constant at 40 °C, 1.0/250 g/mL, and 400 rpm, respectively. The results given in Fig. 1 indicate that the dissolution rate increases when the solution concentration is raised from 0.25 to 1.00 M. Ammonium ions furnish the protons required (in Eq. 4) for the dissolution reaction. Thus, H_3O^+ ion concentration increases with an increase in the concentration of ammonium acetate, and as a result of this, the dissolution rate increases.

Fig. 2 shows the effect of the solid to liquid ratio on the dissolution rate of zinc oxide. These experiments were carried out in the range of 0.5/250-3.0/250 g/mL of solid to liquid ratio. In these tests, the values of the other parameters were kept constant at 40 °C, 0.75 M, and 400 rpm.

This figure shows that the dissolution rate of zinc oxide decreased as the solid to liquid ratio increased. This situation can be explained by the increase in the amount of solid per amount of fluid reagent in the reaction mixture.

To examine the effect of reaction temperature on the dissolution rate of zinc, the experiments were performed in the range of 25-50 °C of temperature. The concentration of ammonium acetate, solid to liquid ratio, and stirring speed were retained constant at 0.75 M, 1.0/250 g/mL, and 400 rpm, respectively.

The results of this parameter are presented in Fig. 3. It is understood that the reaction temperature has a noticeable effect on the dissolution of zinc oxide. It is seen that the dissolution rate increases with an increase in the reaction temperature.

3.3. Kinetic analysis

The rate of dissolution reaction between the solid and liquid reactants can be analyzed by using the heterogeneous and homogeneous reaction models. According to the heterogeneous reaction models, it is considered that the reaction between a solid and solvent occurs on the outer surface of the solid reactant. The solid is initially surrounded by a fluid film through in which mass transfer takes place. As the reaction proceeds, the unreacted core of the solid reactant shrinks towards the center of the solid, and a product layer forms around the unreacted core. When a product layer does not form, the reacting particle shrinks during the reaction and completely dissolves in the solution.

The rate of a non-catalytic heterogeneous reaction can be controlled by diffusion through the fluid film, diffusion through the product layer, or a chemical reaction at the solid particle surface. The derived rate equations for these models have been introduced in the literature (Levenspiel, 1972; Mazet, 1992; Wen, 1968).

In the homogeneous reaction model, the liquid reactant is assumed to enter into the solid particle and react at all times throughout the solid particle. Under these conditions, the reaction rate can be defined by pseudo-homogeneous reaction models, such as first or second order. To determine the kinetic parameters and the rate-controlling step of the dissolution of ZnO in ammonium acetate solutions, the experimental data obtained were analyzed by using the heterogeneous and homogeneous reaction models. After the heterogeneous models were performed to the experimental data, it was determined that these models were not suitable to describe the dissolution reaction. Afterwards, the pseudo-homogeneous reaction models were applied to derive the equation of this dissolution process. The

integrated rate equations for homogeneous model are as follows (Eqs. 9 and 10):

$$-\ln(1-x) = kt \text{ (for the first order pseudo-homogeneous model)} \quad (9)$$

$$(1-x)^{-1} - 1 = kt \text{ (for the second order pseudo-homogeneous model)} \quad (10)$$

If the dissolution reaction follows this model, then the plots of the left side of Eqs. (9 and 10) versus time must be a straight line. When the first and second order rate equations were applied to find the rate equation for this process, it was observed that the experimental data did not fit to the second order rate equation.

Using the first order rate equation, the left side of Eq. (9) was plotted versus the reaction time for different solution concentrations, solid to liquid ratios, and reaction temperatures, respectively. As can be seen from the plots given in Figs. 4-6, the straight lines passing through the origin were obtained. Therefore, the equation representing the kinetics of this dissolution process can be expressed as follows (Eq. 11).

$$-\ln(1-x) = kt \quad (11)$$

To include the effect of the reaction parameters on the reaction rate constant, a semi-empirical model can be written as in Eq. (12):

$$k = k_0 C^a (S/L)^b \exp(-E_a/RT) \quad (12)$$

where: k_0 is the frequency or pre-exponential factor (1/s); C is the concentration (mol/L); (S/L) is the solid-to-liquid ratio (g/mL); E_a the activation energy (J/mol), R is the universal gas constant (J/molK), and T is the reaction temperature (K). Combining Eqs. (11, 12), the Eq. (13) is obtained:

$$-\ln(1-x) = k_0 C^a (S/L)^b \exp(-E_a/RT) t \quad (13)$$

The constants a and b in Eq. (13) were calculated from the apparent rate constants obtained

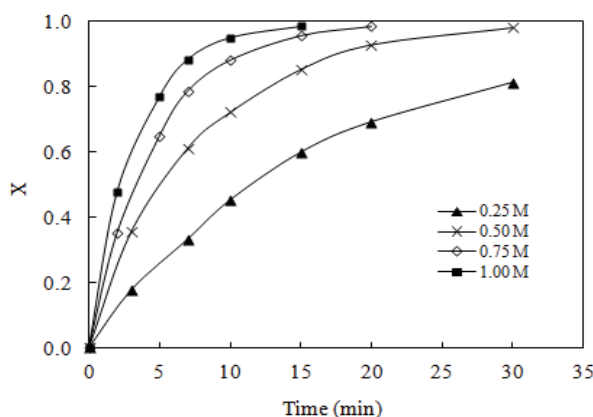


Fig. 1. Effect of ammonium acetate concentration on the dissolution of zinc oxide

from Figs. 4-5. Using the apparent rate constant values obtained from Fig. 4 for the solution concentration, a plot of $\ln k$ versus $\ln C$ was drawn in Fig. 7. The slope of the straight line in Fig. 7 gives the reaction order with respect to the ammonium acetate concentration. The reaction order is proportional to 1.1 power of solution concentration with a correlation coefficient of 0.999. To find the reaction order with respect to the solid to liquid ratio, the apparent rate constants obtained from Fig. 5 were used.

According to the result found, the reaction order is proportional to -0.86 power of solid to liquid ratio. The correlation coefficient for this parameter is 0.991. The temperature dependence of a chemical reaction is expressed by Arrhenius equation. The activation energy of the process can be calculated by using Arrhenius equation. Using the apparent rate constants obtained from Fig. 6, the plot of $\ln k$ versus $1/T$ was constructed in Fig. 8.

The slope of the straight line in Fig. 8 gives the E_a/R value, and the intercept is $\ln k_0$. The values of E_a/R and $\ln k_0$ were found to be 5272 and 15.11, respectively.

From the value of E_a/R , the activation energy of the reaction was calculated to be 43.83 kJ/mol. Diffusion controlled heterogeneous processes are slightly dependent on temperature while chemical controlled processes are strongly dependent on temperature.

Therefore, the value of the activation energy of a dissolution reaction may be used to predict the rate-controlling step (Demirkiran, 2008). The activation energy of a chemical controlled reaction is usually above 40 kJ/mol (Habashi, 1983).

The determined value of the activation energy in this study indicates that the dissolution of zinc oxide in ammonium acetate solutions is controlled by chemical reaction. Consequently, the following kinetic expression including the parameters used in this dissolution process can be written as Eq. (14).

$$-\ln(1-x) = 3.6510^6 C^{1.1} (S/L)^{-0.86} \exp(5272/T) t \quad (14)$$

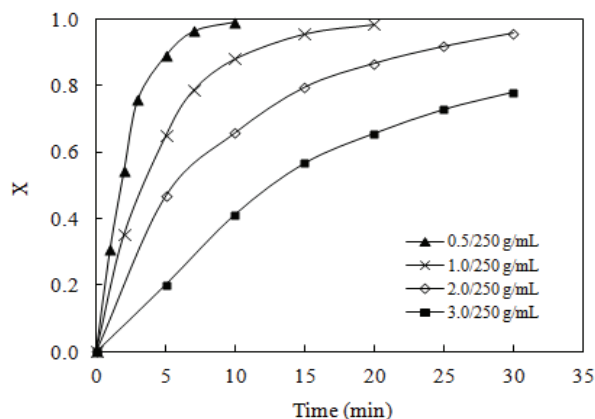


Fig. 2. Effect of the solid to liquid ratio on the dissolution of zinc oxide

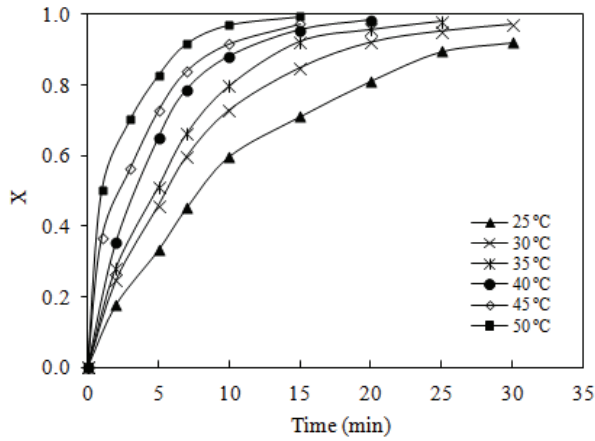


Fig. 3. Effect of the reaction temperature on the dissolution of zinc oxide

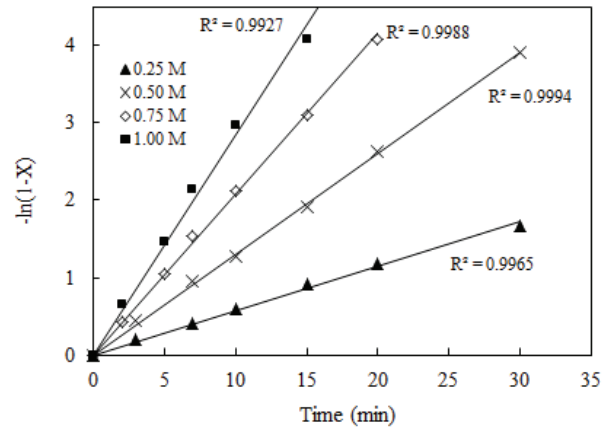


Fig. 4. Plot of $-\ln(1-x)$ versus time for various concentrations

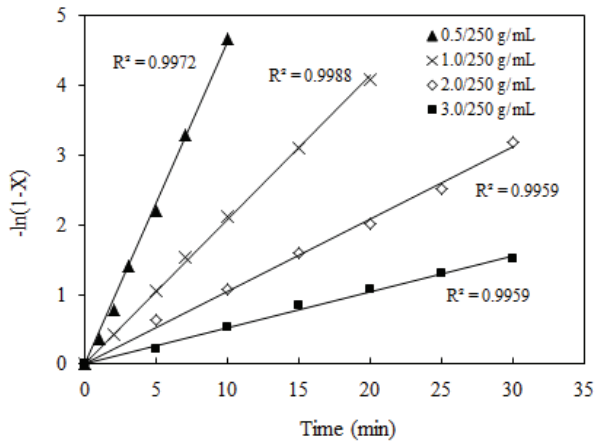


Fig. 5. Plot of $-\ln(1-x)$ versus time for various solid-to-liquid ratios

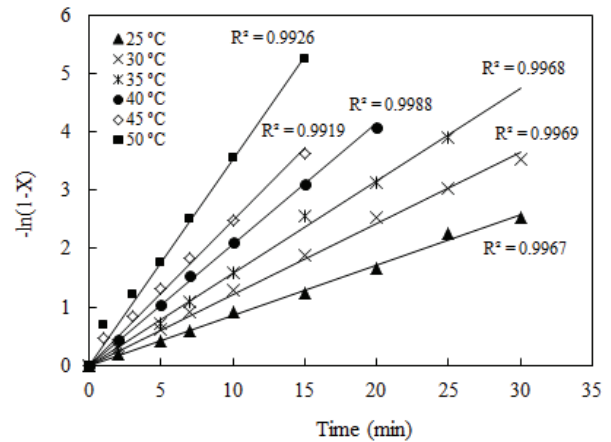


Fig. 6. Plot of $-\ln(1-x)$ versus time for various temperatures

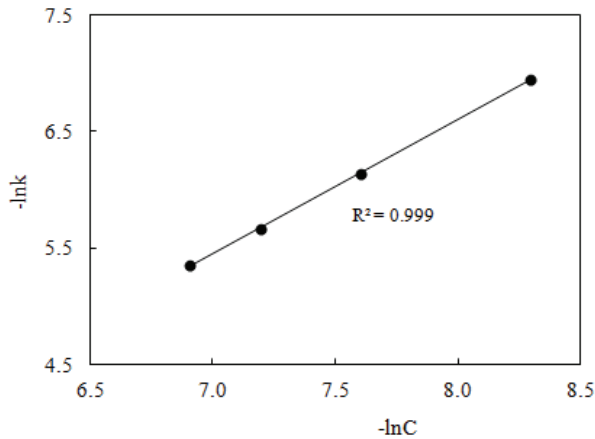


Fig. 7. Plot of $-\ln k$ versus $-\ln C$

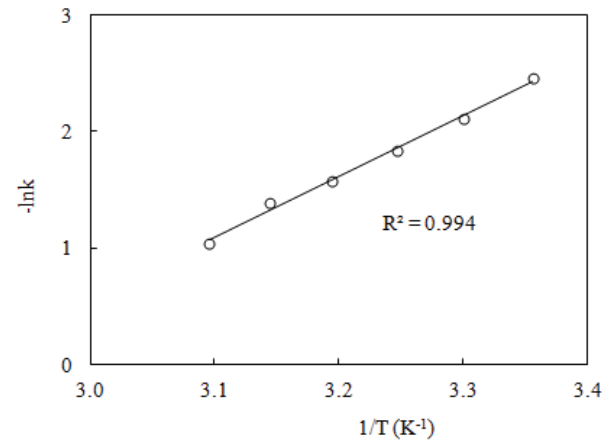


Fig. 8. Arrhenius plot for the dissolution process

4. Conclusion

The following conclusions can be deduced according to the findings obtained from this study:

Ammonium acetate solutions can be effectively used to extract the zinc from the waste battery powder. It was observed that both reaction temperature and ammonium acetate concentration had significant influence on the rate of dissolution of zinc oxide. It was found that the dissolution rate

increased with increasing ammonium acetate concentration and reaction temperature, and with decreasing solid to liquid ratio. It was determined that zinc oxide was dissolved approximately 99.5 % under the experimental conditions at 1 M, 40 °C, 400 rpm, 1/250 g/mL, and 15 min. The kinetic analysis results showed that the dissolution rate fit to the first-order pseudo-homogeneous reaction model. The activation energy of the dissolution process was found to be 43.83 kJ/mol. This activation energy

value indicates that the dissolution of zinc oxide in ammonium acetate solutions is controlled by chemical reaction. However, it should be specify that the results of this study were obtained by using pure zinc oxide. For this reason, if the actual spent battery powder is used in the leaching, then the dissolution behavior and kinetic parameters can be completely different since the solid matrix is different. Nevertheless, the present work can give an opinion about the dissolution behavior of zinc oxide from the battery powder. In the literature, it has been generally used the acidic solvents containing various reductive agent to gain the manganese from the battery powder. Zinc, manganese, and other impurities are dissolved in the solid matrix when these types of solvents are used for the purpose of the leaching. In this case, the separation processes must be applied to recover the zinc and manganese. Providing ammonium acetate solutions a selective leaching for zinc in the waste battery powder, it may eliminate the need for the separation processes. The present study may offer an advantage in this respect.

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MAGNITUDE OF DAMAGE EVENTS ON HYDROTECHNICAL TORRENT CONTROL STRUCTURES

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Abstract

The objectives of this paper address the identification and statistical analysis of the laws underlying the variability of the magnitude of the damages to torrent control structures induced by four of the most well-known events affecting their stability, resistance and durability. The research set consists of 100 torrent control structures that have continuously functioned for almost three decades in a managed torrential watershed in the forested mountainous area of Romania. In the first stage, the criteria and quantitative assessment scales regarding the magnitude of the damage that occurred during this period are set. In the second stage, a statistical analysis is performed aiming at fitting frequency distributions to the magnitude of these events. Quantification of the magnitude is presented by means of two statistical indicators (arithmetic mean and variation coefficient) as well as in the form of a theoretical function that can be used to estimate the frequency of events of various intensities over the entire functional period of the structures. On a 5-degree intensity scale (1=very low; 5=very high), three of the researched events (breakage of the terminal spur, undermining of the body, undermining of the apron) were of medium intensity, and the fourth (erosive damage or abrasion) was of low intensity. The statistical variability of the magnitude of the damage, as well as the nature of the law followed by the frequency distributions of the damage magnitudes, depends on: the nature of the event, the characteristics used for the quantification of the magnitude and the amplitude of the interval used for grouping frequencies into classes. Charlier type A and Beta laws have proved their flexibility in fitting the sequences of experimental frequencies, even if the values of the magnitude variation coefficient ranged, due to the influence of several factors, from 30% to 70%. From a practical point of view, the results can guide future monitoring and maintenance decisions concerning the type, extent and periodicity of the operations ensuring: the required performance of torrent control structures, the reinstatement of the structures affected by stream processes and the reestablishment of systems of which they are part.

Key words: apron undermining event, body structure undermining event, breakage event, erosive damage event

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1. Introduction

In response to the Commission Directive 2007/60/EC on the assessment and management of flood risks and with regard to the requirements imposed by the new generation of programmes and projects in the field of torrential integrated hydrologic watershed management (FAO, 2004, 2005; SAEFL, 2003), the scientific research in this field has recently focused on matters concerning flood risk management (Badaluta-Minda and Cretu, 2010; Bressers and Lulofs, 2010; Grozavu et al.,

2013; Heinimann, 2003; Ministry of Environment, 2009), on emphasising the environmental impact and the efficiency of retention dams (Castillo et al., 2007; Conesa-García and García-Lorenzo, 2008; Remaitre et al., 2008; Surian and Rinaldi, 2003; Xiang-zhou et al., 2004) and on an integrated monitoring of the hydrotechnical torrent control structures (Clinciu, 2005; Clinciu and Gaspar, 2005; Davidescu et al., 2012; Giurma-Handley et al. 2010; Lazar and Gaspar, 1994; Mazzorana and Fuchs, 2010; Polyakov et al., 2014; Quiñonero-Rubio et al., 2014). The primary goals are: maintenance of structures within

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the managed torrential network of small, predominantly forested watersheds, reinstatement of those structures affected by stream process, and reestablishment of the systems of which they are part of.

Supporting scientific research regarding statistical analysis of damage patterns can contribute to a better implementation of systematic and permanent monitoring and maintenance of torrent control structures (Clinciu et al., 2010a, 2010b; Giurgiu, 1972; Petrișan and Clinciu, 2009).

By focusing on this goal, this paper continues earlier research initiated to ground the monitoring of torrent control structures on a statistical basis (Clinciu et al., 2010a). This time the purpose is to highlight, on the basis of the developed methodology, the magnitude of the four most dangerous damage patterns: the breakage event, the erosive damage event, the body structure undermining event; and the apron undermining event.

The objectives of this research focus on providing the answers to three scientific questions:

- What is the average magnitude of the events classified as damages?

- How large is the variation of the intensity of damages during the functional period of the structures?

- What are the theoretical laws behind the variation of damage intensity?

Answering these questions is important because predictive knowledge regarding the nature, frequency and average magnitude of damage patterns, allows the central public authority for silviculture to make decisions with respect to the nature, volume and periodicity of operations ensuring: the maintenance of torrent control structures, the reinstatement of those structures affected by stream processes, and the security of systems of which they are part.

On the other hand, it is only after gaining knowledge about the laws underlying statistical variability, that the public decision maker can rely on frequency estimates associated with the intensity of various structural damage patterns in hydrographic watersheds, similar to the one researched, in terms of: surface area and degree of afforestation, pluviometric regime, construction characteristics and functional period of the structures, nature and quality of construction materials, applied execution technologies, etc.

2. Datasets and methods

The datasets are identical to that used in previous research (Clinciu et al., 2010a). The 100 structures built along 21 torrential valleys in the Upper Târlung Watershed (about 190 km²), upstream of the Săcele water storage-Brașov county (25° 48' E, 45° 30' N) (Fig. 1), were considered. Out of these structures: dams are the most numerous (55, but only 49 of them were taken into account since 6 dams have been totally destroyed by a torrential event),

traverses and sills are almost equally represented (23 and 22 respectively), and canals are very poorly represented (only 4).

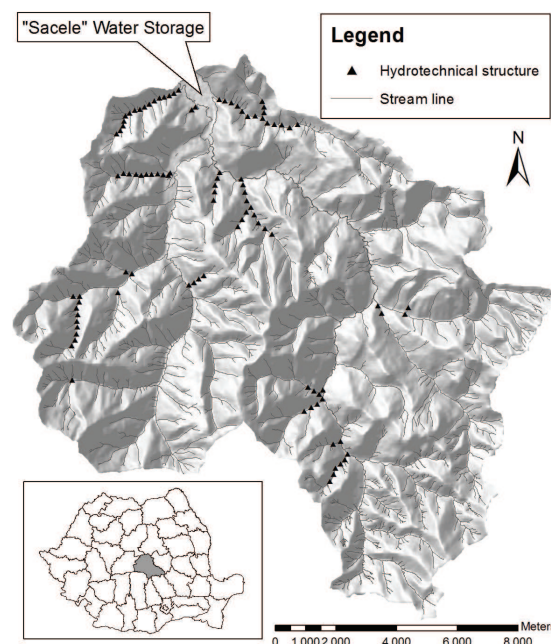


Fig. 1. Location of the hydrotechnical structures on the managed torrentials valleys

The mountainous area where the 21 managed torrential valleys are located is predominantly grafted on sedimentary rocks (lime and grit stones) and it lies from 730 m to 1875 m. The average annual precipitation is between 800 mm and 1800 mm. The drainage area of watersheds where are located hydrotechnical structures varies from 37 ha to 1393 ha, the afforestation degree from 50% to 96%, and the average slope gradient is 20% ... 40%.

A statistical approach was developed for the magnitude of behavioural events in the category of damage patterns. In the first research stage, this magnitude was quantified by two characteristics in the case of each one of the four researched events, along with definitions of the corresponding scales, subsequently followed by quantification proper (these characteristics are different for each event, see details in Tables 1-3, 5). Depending on the direction of the intensity increase on each scale, the cells resulting from the intersection of the used scale intervals are grouped into five zones each expressing a certain degree of the global magnitude of damage (the same number of cells characterises each of five zones), ranging from very low global magnitude (in the upper left part of the Tables 1, 2, 3 and 5) to very high global magnitude (in the bottom right part of the same table). By weighting these degrees (I_i) by the sum of the frequencies corresponding to each area (n_i), the global average magnitude of each researched event (K_{damage}) is estimated using Eq. (1):

$$K_{damage} = \sum_{i=1}^5 I_i \cdot n_i \quad (1)$$

In the second research stage, in order to find the variation of the magnitude of damage patterns and the law underlying this variation, frequency distributions of the damage magnitudes for the affected structures, obtained separately for each individual criterion and for the global criterion resulting from the combination of these individual criteria, are subjected to statistical study both in terms of the main statistical indicators and the possibility of fitting by three of the most well-known theoretical distributions (normal, Charlier type A and Beta).

The data was processed using STATISTICA 8.1. software (Statsoft Inc., 2005) and the results were compiled for each criterion separately, in fields of composed figures each comprising three component parts: the curves of the theoretical and experimental frequencies, the values of the main statistical indicators (m-arithmetic mean, s%-variation coefficient), and the (theoretical and experimental) values of the χ^2 test for the above mentioned theoretical distributions. The χ^2 value was specified for each type of distribution mentioned. This value was computed using Eq. (2):

$$\chi^2 = \sum \frac{\left(\hat{n} - n \right)^2}{\hat{n}} \quad (2)$$

where n is the experimental frequency, and $\hat{n}$ is the theoretical frequency.

3. Results and discussions

The four damage patterns are analysed referring to frequencies and the degree of magnitude. Descriptive and illustrative elements regarding these damage patterns can be found in details in Clinciu et al. (2010 a).

3.1. Breakage event

3.1.1. Introductory elements

During the studied period 34 transverse structures and 47 component parts were affected by a

breakage event. Only two of the affected structures are traverses (out of a total of 23), 8 are sills (out of 22), and 24 are dams (out of 49). Thus, the degree of damage is as follows: 8% for traverses, 36% for sills, and 49% for dams.

When compared to the total number of structures (Fig. 2), it has been noted that sills affected by breakage are equally represented (23%), while the degree of damage differs from the degree of representation in the case of dams and traverses: it is much higher for dams (71% as opposed to 51%) and much lower for traverses (6% as opposed to 26%).

The parts most affected by a breakage event are: the apron zone terminal spur, identified in 24 cases (51%), and the energy dissipation teeth, identified in 13 cases (28%). The breakage event rarely occurs in the other 7 component parts; it was recorded only once in 5 parts, twice in one part and three times in another part.

3.1.2. Breakage of the terminal spur

The following two criteria are considered in order to estimate the global magnitude of this event:

- the depth along which breakage occurred, classified by the following degrees: 0.0–0.5 m; 0.5–1.0 m; 1.0–1.5 m; 1.5–2.0 m; 2.0–2.5 m.
- the proportion of the apron length on which breakage occurred, quantified by classes of 10 percent (0–10%, 10–20%,, 90–100%).

In order to combine the two criteria in the table of cells, showing the frequencies associated to a breakage event in the intersection areas of the degrees of the two individual criteria (Table 1), five distinct areas (each containing 10 cells) were delimited, each area being characterised by a certain global magnitude of damage, ranging from very low (in the upper left part of the table) to very high (in the bottom right part of Table 1).

The distribution of the identified cases on the intensity scale is as follows:

- (1) – very low intensity: 6 cases;
- (2) – low intensity: 5 cases;
- (3) – medium intensity: 2 cases;
- (4) – high intensity: 2 cases;
- (5) – very high intensity: 9 cases.

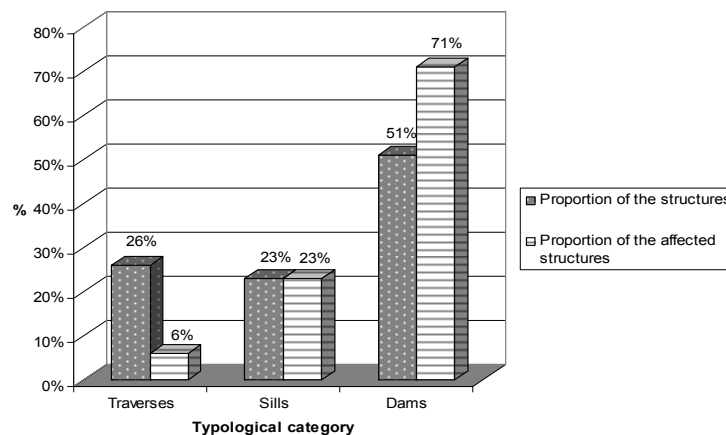


Fig. 2. Comparative percentage frequencies for the researched structures (left) and the structures affected by breakages (right)

Table 1. Frequency zoning for the terminal spur breakage event

Proportion of breakage (%)	Depth of breakage (m)					Total
	0.0...0.5	0.5...1.0	1.0...1.5	1.5...2.0	2.0...2.5	
0 ... 10	0	0	0	0	0	0
10 ... 20	1	1	0	0	0	2
20 ... 30	0	1	2	0	0	3
30 ... 40	0	2	1	0	0	3
40 ... 50	1	1	0	0	0	2
50 ... 60	0	1	0	0	0	1
60 ... 70	0	1	1	1	0	3
70 ... 80	0	1	0	0	0	1
80 ... 90	0	0	1	0	0	1
90... 100	0	0	3	4	1	8
Total	2	8	8	5	1	24

The coefficient of the global magnitude of the researched event, having the value as presented in Eq. (3) shows that the breakage of the apron zone terminal spur occurred as a behavioural event of medium magnitude.

$$K_R = \frac{6 \cdot 1 + 5 \cdot 2 + 2 \cdot 3 + 2 \cdot 4 + 9 \cdot 5}{24} = 3.1 \approx 3 \quad (3)$$

The statistical laws followed by the magnitude of this event were examined based on three frequency distributions:

- the frequency distribution of breakages of the terminal spur (in the apron zone) by categories of depth along which breakage occurred;
- the frequency distribution of the same breakages, by categories of proportion of the apron length on which breakage occurred;
- the frequency distribution of breakages by degrees of the global magnitude of the event, the classification of the magnitude being made on a scale with 5 classes, from 1 (very low intensity) to 5 (very high intensity).

On this intensity scale (Fig. 3) the global average magnitude of breakage is 3.12, while the variation coefficient for the first two frequency distributions lies from 44% to 49%, and it rises to 55% in the case of the third one. Regarding the concordance between the experimental frequency distributions and the theoretical frequency distributions, the χ^2 test shows the following (Fig. 3):

- for the frequency distribution of the depth of breakage, the law of the behavioural event is well reflected by all three theoretical distributions that were considered, and the goodness-of-fit (estimated by means of the $\chi^2_{\text{exp}}/\chi^2_{\text{theor}}$ ratio) leads to the following hierarchy of distributions: normal distribution, Charlier type A distribution, and Beta distribution;

- in case of the proportion of the breakage length, Beta and Charlier type A distributions (in this order) show their flexibility, both being a good fit, but normal distribution could be shown;

- finally, the fit is limited only to the theoretical Beta distribution, in the case of the global magnitude of the event.

3.2. Erosive damage event

The detailed analysis upon the damage of the hydrotechnical structures by water and alluvia, regards only the body of the overflowed area, which was identified as having the highest frequency of damage.

If the depth of the erosive damage is estimated on the scale proposed by Lazăr and Gaspar (1994) (up to 10 cm = superficial erosive damages; over 10 cm = deep erosive damages), the data is distributed as follows: superficial erosive damages - 39 cases (83%), deep erosive damages - 8 cases (17%).

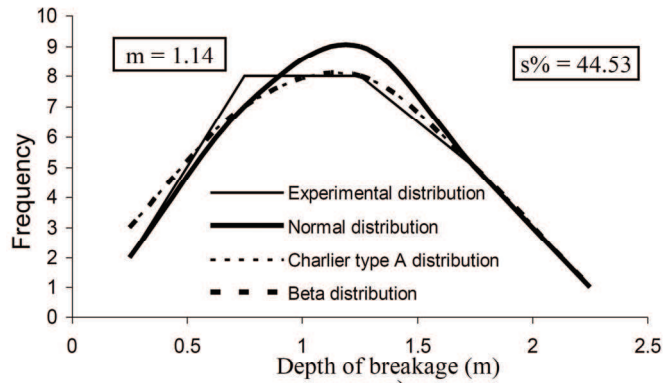
On a more detailed scale, proposed in the present research (1-5 cm = very superficial erosive damages; 5-10 cm = superficial; 10-15 cm = medium deep; 15-20 cm = deep; over 20 cm = very deep), the identified cases of erosive damages are distributed as follows: very superficial - 23 cases (48%), superficial - 17 (35%), medium deep - 2 (4%), deep - 2 (4%), very deep - 4 (9%).

From the point of view of the percentage of damage of the structure part (the body of the overflowed area), the same data reveals the following frequencies:

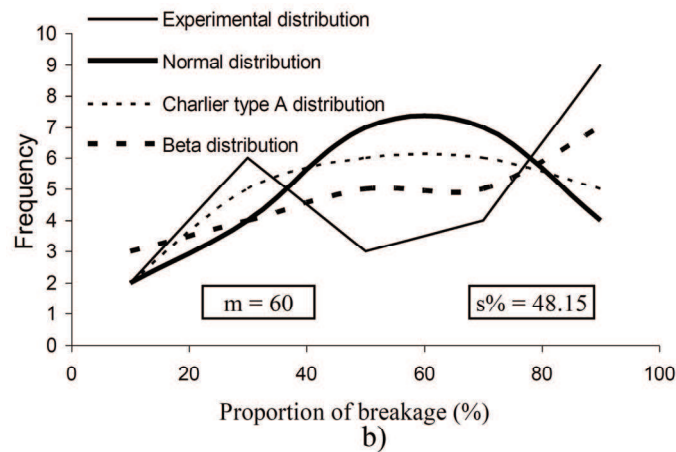
- very low (up to 20% of the surface): 24 cases (51%);
- low (20-40%): 8 cases (17%);
- medium (40-60%): 10 cases (21%);
- extensive (60-80%): 2 cases (4%);
- highly extensive (80-100%): 3 cases (6%).

Thus, quantifying the intensity by the two individual criteria in turn, the study revealed that only 13% of the cases of erosive damage in the overflowed area are deep or very deep and only 10% of these cases display extensive or highly extensive damaged surfaces.

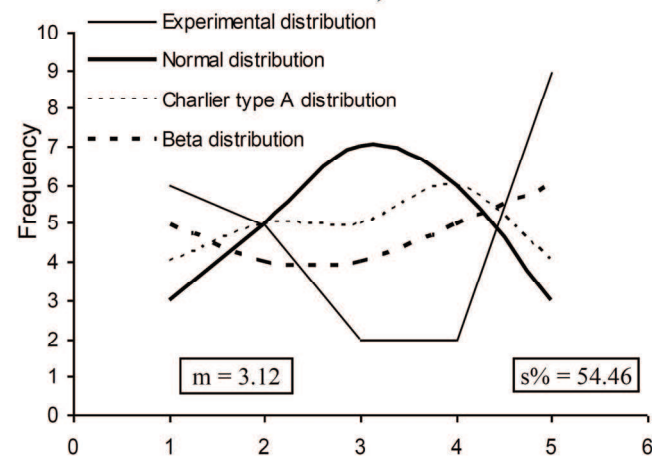
The same method as in the previous case (Table 2) was applied in order to combine the criteria, and the following distribution was discovered with respect to the identified cases by the five degrees of intensity used in this research: (1) very low intensity: 35; (2) low intensity: 7; (3) medium intensity: 3; (4) high intensity: 1; (5) very high intensity: 2.



χ^2 test		
Theoretical distribution	Experimental value	Theoretical value
Normal	0.25	9.48
Charlier, type A	0.47	9.48
Beta	0.47	7.81
Conclusion: All three theoretical distributions fit the experimental distribution.		



χ^2 test		
Theoretical distribution	Experimental value	Theoretical value
Normal	10.82	9.48
Charlier, type A	5.56	9.48
Beta	2.91	7.81
Conclusion: Charlier – type A and Beta theoretical distributions fit the experimental distribution		



χ^2 test		
Theoretical distribution	Experimental value	Theoretical value
Normal	21.23	9.48
Charlier, type A	11.71	9.48
Beta	4.75	7.81
Conclusion: The experimental distribution follows the law of Beta distribution		

Fig. 3. The experimental frequency polygons, the theoretical frequency curves, the values of the main statistical indicators and the χ^2 test values for the distributions studied in the case of breakages occurring in the terminal spur (apron zone): a) by categories of depth of breakage in the apron zone; b) by categories of proportion of the apron length on which breakage occurred; and c) by degrees of global magnitude of the event

For two out of the three criteria, used in the analysis of the intensity, two frequency distributions, different from the point of view of the amplitude of the class interval, were formed and studied for each one as follows:

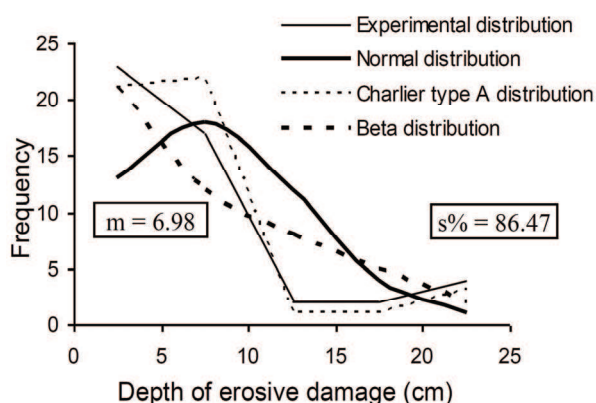
- for the "depth of the erosive damage" criterion (Fig. 4), the class intervals of 5 and 10 cm were considered respectively;
- for the "proportion of the affected surface" criterion (Fig. 5), the amplitude of 10% and 20% were considered respectively.

In case of the criterion concerning the global magnitude of damage (Fig. 6), the frequencies were grouped according to 5 degrees of intensity, ranging from 1-very low intensity up to 5-very high intensity.

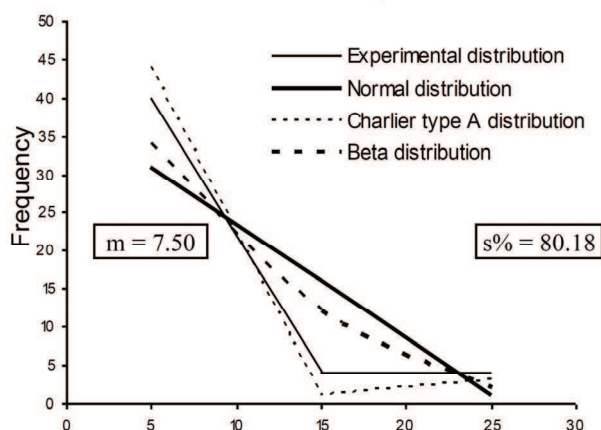
Consequently, following the functioning of the structures for approximately 25 years, the average depth of erosive damage was approximately 7 cm, and it affected on average approximately 30% of the surface. The global average magnitude obtained was approximately 1.5.

Table 2. Frequency zoning regarding the extent of erosive damages

Proportion (%)	Depth (cm)					Total
	1-5	5-10	10-15	15-20	Over 20	
0 ... 10	4	4	1	0	0	9
10 ... 20	6	6	1	1	1	15
20 ... 30	3	4	0	0	0	7
30 ... 40	0	1	0	1	0	2
40 ... 50	6	1	0	0	1	8
50 ... 60	1	1	0	0	0	2
60 ... 70	2	0	0	0	0	2
70 ... 80	0	0	0	0	0	0
80 ... 90	0	0	0	0	0	0
90... 100	1	0	0	0	2	3
Total	23	17	2	2	4	48



a)

 χ^2 Test

Theoretical distribution	Experimental value	Theoretical value
Normal	26.08	9.48
Charlier, A type	3.66	9.48
Beta	10.57	7.81
Conclusion: The experimental distribution follows the law of Charlier - type A distribution		

 χ^2 Test

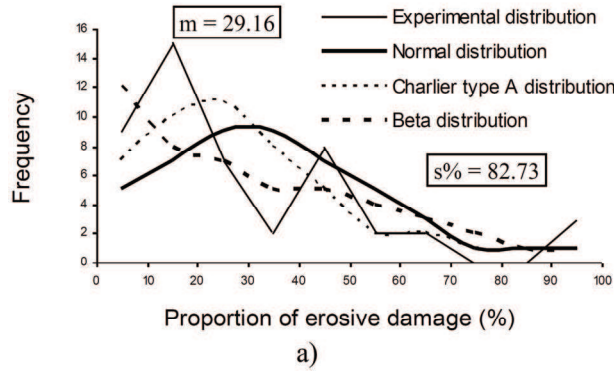
Theoretical distribution	Experimental value	Theoretical value
Normal	20.61	5.99
Charlier, A type	9.69	5.99
Beta	8.39	3.84
Conclusion: The experimental distribution does not follow any of the three theoretical distribution		

Fig. 4. The frequency distributions regarding the extent of the erosive damage of the structures, formed according to the “depth of the damage” criterion: a) classes with an amplitude of 5 cm; b) classes with an amplitude of 10 cm

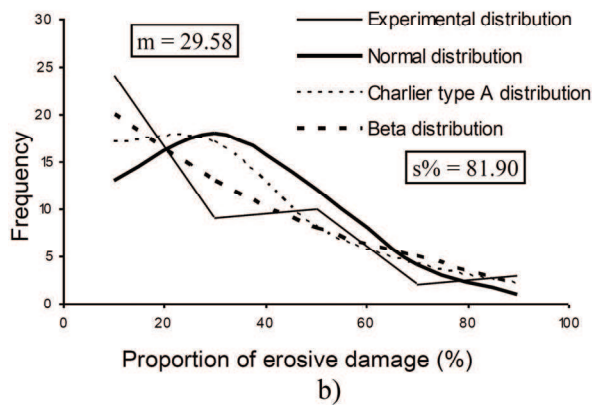
The high value of the variation coefficient, both for the depth of erosive damage (80-86%) and the extent of the affected surface (81-83%), shows that the event magnitude variation was a significant one. Grouping the frequencies into classes with a different amplitude led to important changes of the variation coefficient only in the case of the global magnitude of damage (67% and 45%), while, for the other criteria, the value of the afore mentioned coefficient showed little variation, both for the depth of erosive damage (86% and 80%) and the extent of the surface affected by erosive damage (83% and 82%).

The application of the χ^2 test, separately for each research variant, proved that the experimental distribution of the depth of erosive damage follows the law of Charlier type A distribution, but only when frequencies are grouped into classes with an amplitude of 5 cm. In the case of the classes with an amplitude of 10 cm, the experimental frequency does not follow any of the three theoretical distribution patterns. In both situations, distributions are very far from normal distribution. In the case of the proportion of the affected surface, the experimental distribution also does not correspond to the normal

distribution. Here, the variation of the event magnitude is well rendered either only by the law of Charlier type A distribution, when frequencies are grouped into classes with an amplitude of 10%, or by both the law of Charlier type A distribution and the law of Beta distribution, when frequencies are grouped into classes with an amplitude of 20%. For the global magnitude of damage, the sequence of experimental frequencies follows only the law of Charlier type A distribution; this distribution is also very far from normal distribution.

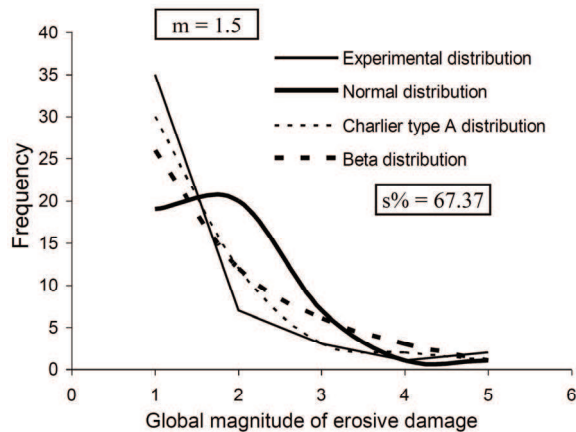


χ^2 test		
Theoretical distribution	Experimental value	Theoretical value
Normal	26.51	16.91
Charlier, type A	16.82	16.91
Beta	18.81	15.51
Conclusion: The experimental distribution follows the law of Charlier type A distribution		



χ^2 test		
Theoretical distribution	Experimental value	Theoretical value
Normal	19.14	9.48
Charlier, type A	8.64	9.48
Beta	4.83	7.81
Conclusion: The experimental distribution follows the law of Charlier type A and Beta distributions		

Fig. 5. The frequency distributions regarding the extent of the erosive damage of the structures, formed according to the “proportion of the affected surface” criterion: a) classes with an amplitude of 10%; b) classes with an amplitude of 20%



Theoretical distribution	Experimental value	Theoretical value
Normal	25.20	9.48
Charlier, type A	4.41	9.48
Beta	9.03	7.81
Conclusion: The experimental distribution follows the law of Charlier type A distribution		

Fig. 6. The frequency distributions regarding the extent of the erosive damage of the structures, established by the five degrees of the “global magnitude of damage” (very low, low, medium, high and very high)

Finally, comparing Charlier type A and Beta distributions (recognised for their flexibility) in terms of the quality of fitting, Charlier type A distribution was noted to be the best fit, especially if the amplitude of class interval is decreased.

3.3. Body structure undermining event

The cases affected by this event, a total of 7, refer exclusively to traverses (totalling 25) and are distributed in 10 out of the 21 managed torrential valleys. By comparing the proportion of damage and the proportion of typological representation of the structures (Fig. 7), one can notice that, overall, traverses represent only 24%, but they are affected to an extent which is almost three times higher (68%).

In order to estimate the global magnitude of damage, similar criteria to those used in the analysis of the magnitude of the breakage event were taken into consideration:

- the depth of the undermining, by degrees of 0.5 m, and
- the degree of damage to the body of the structure, along its length, by percentage classes with an amplitude of 10%.

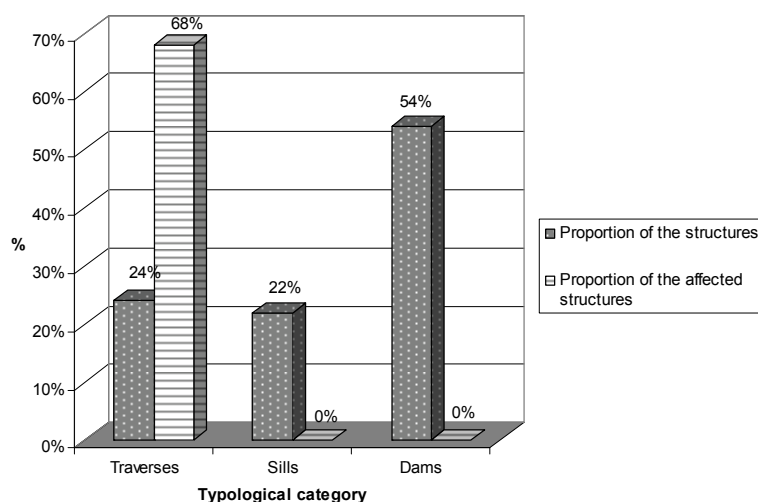


Fig. 7. Comparison between the proportion of damage and the proportion of representation, for the event concerning the undermining of the body of traverses

Table 3. The frequencies of the traverses affected by the body undermining

Proportion of body undermining (%)	Depth of body undermining (m)				Total
	0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	
0-10	0	0	0	0	0
10-20	0	0	0	0	0
20-30	0	0	0	0	0
30-40	1	1	1	0	3
40-50	0	3	2	0	5
50-60	0	1	0	0	1
60-70	1	0	0	1	2
70-80	0	0	1	0	1
80-90	0	0	0	0	0
90-100	2	1	0	0	3
Total	4	6	4	1	15

Depending on these two criteria, the traverses affected by the undermining of the body are distributed as shown in Table 3. By adding the frequencies found in the cells pertaining to the same area, the following distribution was obtained with respect to the degrees taken into consideration for characterising the global intensity of the event: (1) very low intensity 1 case; (2) low intensity 5 cases; (3) medium intensity 4 cases; (4) high intensity 4 cases; (5) very high intensity 1 case.

By assigning weights to the intensity degrees and by adding the products of these weights and the corresponding frequencies, this coefficient was obtained (Eq. 4):

$$K_{sc} = \frac{1 \cdot 1 + 2 \cdot 5 + 3 \cdot 4 + 4 \cdot 4 + 5 \cdot 1}{15} = 2.93 \approx 3.00 \quad (4)$$

which shows that the undermining of the body of a traverse was a medium-intensity event.

The statistical analysis of frequency distributions (Fig. 8) proved that the average depth along which the undermining of the body occurred is 0.81 m, and the average proportion of affected body length is 58%.

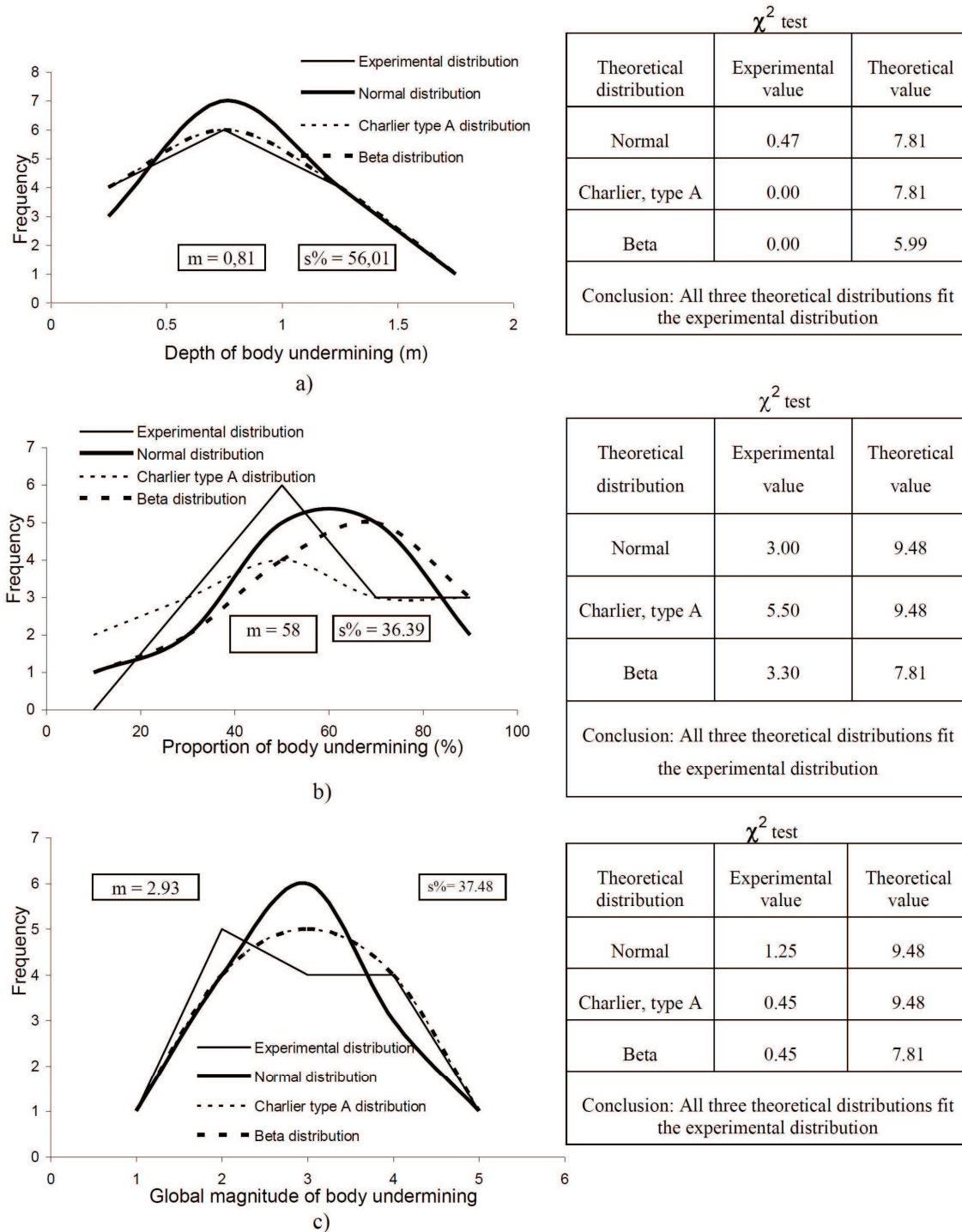


Fig. 8. The experimental frequency polygons, the theoretical frequency curves, the values of the main statistical indicators and the χ^2 test values for the distributions regarding body undermining: a) by degrees of depth of body undermining; b) by categories of proportion of damage to the length of the body; c) by degrees of global magnitude of damage

The distribution obtained for the criterion regarding the depth of the undermining of the body registers the highest variation coefficient (56%). Lower than this (approximately 37%) is the variation coefficient which resulted for the other two criteria.

The χ^2 test, applied separately to each case, proved that the three theoretical distributions used in this analysis fit the experimental distributions, for all the three characteristics that were considered (depth of body undermining, proportion of damage to the

length of the body and global magnitude of event occurrence).

The quality of fitting (estimated by means of the $\chi^2_{\text{exp}}/\chi^2_{\text{theor}}$ ratio) gives the following hierarchy of the theoretical distributions: for the first characteristic, Beta distribution, Charlier type A distribution and normal distribution; for the second characteristic, normal distribution, Beta distribution and Charlier type A distribution; and for the third

characteristic, Charlier type A distribution, Beta distribution and normal distribution.

Consequently, for the magnitude of the behavioural event concerning the undermining of the body of traverses, the normality of the frequency distribution could be statistically shown for all the three characteristics taken into consideration when forming the distributions.

3.4. Apron undermining event

This event was identified in 42 out of 78 transverse structures endowed with apron, 59% (13 cases) of the sills and 53% (29 cases) of the dams were affected.

By comparing the proportion of damage and the proportion of representation (Fig. 9), one can easily note that the highest difference is displayed by the category of sills. Apparently, the result contradicts expectations, since for the category of dams, the degree of damage (53%) is placed below the level of typological representation of the structures in this category (71%).

A possible explanation could be that, in the category of sills, the energy dissipation teeth were included only in 50% of the structures constructed, while the implementation of this dissipation system was carried out to a much larger extent (76%), in the case of dams. Indeed, the re-centralisation of the data revealed that only 6 sills are provided with energy dissipation teeth (46%) out of the 13 affected by apron undermining.

In other words, was slightly higher the proportion of apron undermining in the case of sills of which the apron was not provided with energy dissipation teeth.

On the other hand, as the name "*apron undermining*" encompasses an event localised downstream of the terminal spur of the structure, both in the apron segment and in the two lateral segments (left and right of the apron), the frequency of occurrence of the event was also analysed depending on the positioning of these two component parts of the structures.

The most affected part was the right apron zone spur, identified in 41 cases, while the next on the list, namely the left terminal spur, was identified only in 3 cases and the right terminal spur in only one case (Fig. 10).

The fact that undermining represents one of the causal factors of breakages is suggested by the data shown comparatively in the same figure, where it can be noted that, whereas for the right and the left terminal spur the frequency is similar, for the apron zone terminal spur the frequency is considerably different. It is assumed that this difference is due to the sequence of events because once undermining occurs at the base of the apron favourable conditions for breakage, in the terminal spur on this section of the structure, (also) develop.

In order to prove the formulated hypothesis, rank correlation was applied in order to study the correlative dependence between the number of structures affected by apron undermining, and the number of structures affected by breakage of the terminal spur in the apron zone (Table 4).

The result obtained (a very significant correlation coefficient – Table 4) confirms the assumption that the analysed behavioural events are strongly correlated. Consequently, one can state that apron undermining is the event which determines terminal spur breakage on this section of the structure.

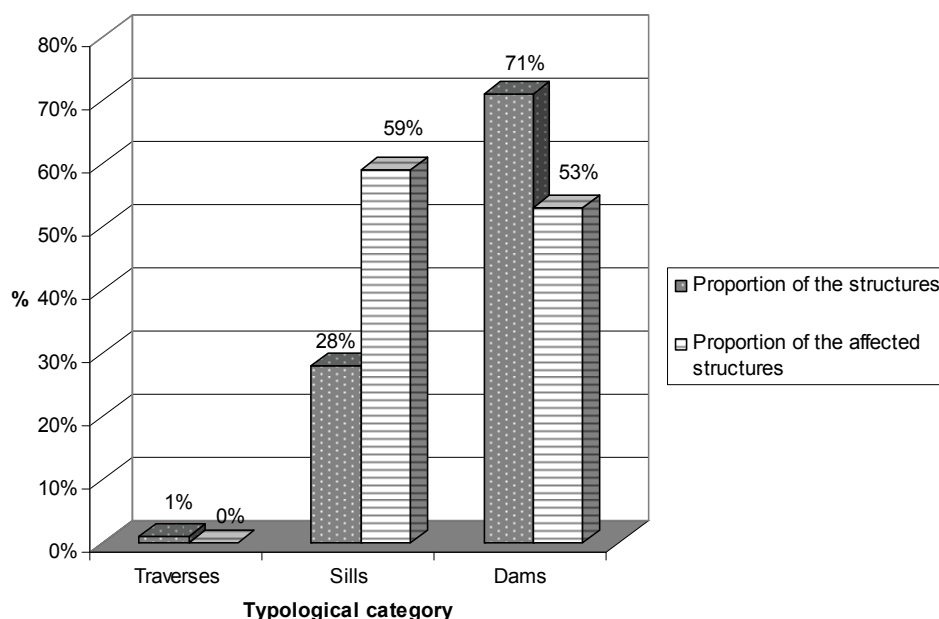


Fig. 9. Comparison between the proportion of damage and the proportion of representation, for the event concerning the apron undermining

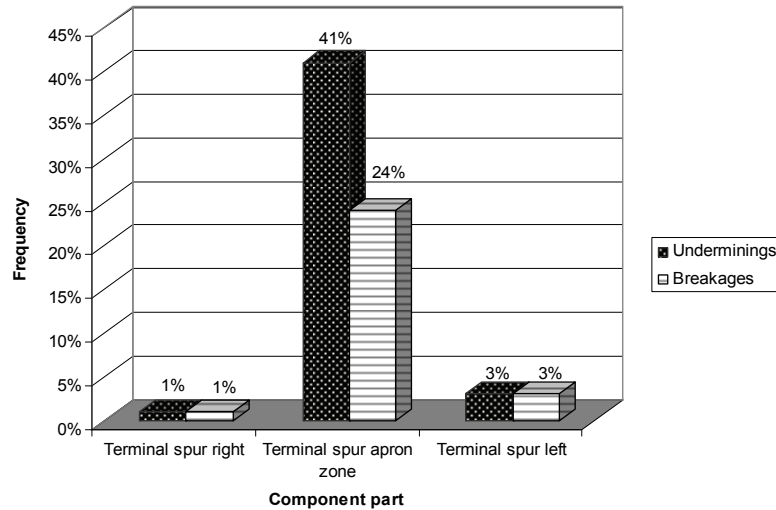


Fig. 10. Comparative presentation of the frequencies of events concerning apron undermining and breakage of the terminal spur in the apron zone

Table 4. Rank correlation between the number of structures with undermining and the number of structures with breakage

Number of:		The rank by:		Difference:	
Underminings	Breakages	Underminings	Breakages	d	d ²
1	0	7.5	9	1.5	2.25
8	4	2	3	1	1
4	2	5.5	6	0.5	0.25
7	4	3	3	0	0
4	3	5.5	5	0.5	0.25
5	5	4	1	3	9
0	0	9.5	9	0.5	0.25
9	4	1	3	2	4
0	0	9.5	9	0.5	0.25
1	1	7.5	7	0.5	0.25
Σ					17.50
$r_s = 1 - \frac{6\Sigma d^2}{n(n^2 - 1)} = 1 - \frac{6 \cdot 17.5}{10(100 - 1)} = 0.894^{***}$					
To f = n - 2 = 10 - 2 = 8 degrees of liberty: $r_{0.001} = 0.872 < 0.894$					

Table 5. The frequencies for each of the 5 areas of the same apron undermining

Proportion of apron undermining (%)	Depth of apron undermining (m)				Total
	0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	
0-10	2	0	0	0	2
10-20	1	1	0	0	2
20-30	0	2	4	0	6
30-40	0	2	1	0	3
40-50	4	1	0	1	6
50-60	2	1	0	0	3
60-70	0	2	1	1	4
70-80	0	1	0	0	1
80-90	0	0	1	0	1
90-100	0	1	4	4	9
Total	9	11	11	6	37

Only the right apron zone spur (the most affected) was subjected to the statistical analysis of the magnitude of the apron undermining event, taking into consideration the following criteria:

- the depth of the undermining in the apron zone by degrees of 0.5 m;

- the proportion of damage to the apron, estimated along its width, by intervals with an amplitude of 10%.

In order to combine the two criteria with a view to characterising the global magnitude of damage, each of the frequencies identified for apron

undermining was placed in the corresponding cell in Table 5, and by successively adding the frequencies for each of the 5 areas of the same damage magnitude, the following case distribution was found:

- (1) - very low intensity 10 cases (27 %);
- (2) - low intensity 9 cases (24 %);
- (3) - medium intensity 4 cases (11 %);
- (4) - high intensity 4 cases (11 %);
- (5) - very high intensity 10 cases (27 %).

The coefficient resulting by assigning weights to the five degrees of intensity is according to Eq. (5):

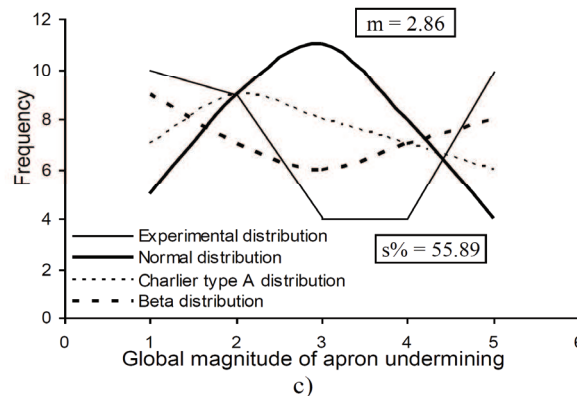
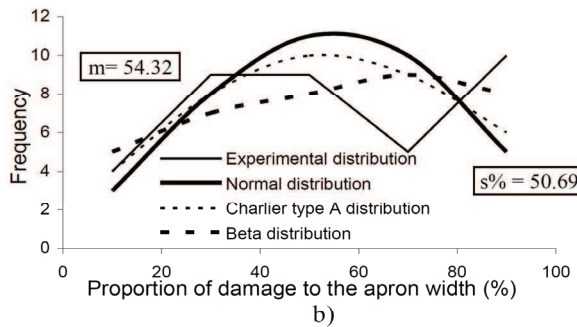
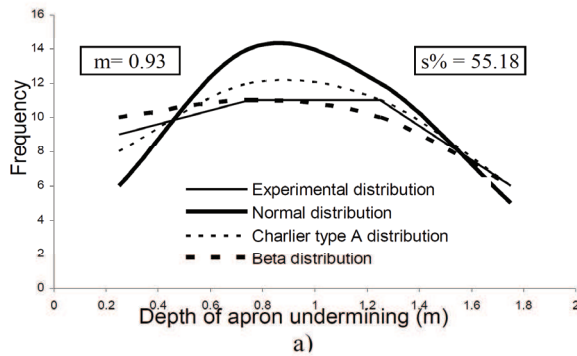
$$K_{Sr} = \frac{1 \cdot 10 + 2 \cdot 9 + 3 \cdot 4 + 4 \cdot 4 + 5 \cdot 10}{37} = 2.86 \approx 3 \quad (5)$$

which shows that apron undermining was a medium-intensity event during the functional period of the structures.

A detailed statistical analysis of the three distributions (Fig. 11) showed that the average depth along which the apron undermining occurred is 0.93 m, and the average proportion of the apron width affected by undermining is 54%.

Both in the case of individual use of analysis criteria and in the case of combined use of these criteria, the values that resulted in the variation coefficient of the event magnitude were close (between 51% and 56%).

The χ^2 test, applied separately for each sequence of frequencies, showed that the experimental distributions are in concordance with the theoretical distributions only for the first two research characteristics of the magnitude (i.e. depth of apron undermining and proportion of damage to the apron width). Concerning the global magnitude of the event, the experimental distribution follows only the laws of Charlier type A and Beta distributions.



χ^2 test

Theoretical distribution	Experimental value	Theoretical value
Normal	2.42	7.81
Charlier, type A	0.90	7.81
Beta	0.20	0.55
Conclusion: All three theoretical distributions fit the experimental distribution		

χ^2 test

Theoretical distribution	Experimental value	Theoretical value
Normal	8.32	9.48
Charlier, type A	4.66	9.48
Beta	3.17	7.81
Conclusion: All three theoretical distributions fit the experimental distribution		

χ^2 test

Theoretical distribution	Experimental value	Theoretical value
Normal	20.45	9.48
Charlier, type A	7.23	9.48
Beta	3.13	7.81
Conclusion: the experimental distribution follows the laws of Charlier type A and Beta distributions		

Fig. 11. The experimental frequency polygons, the theoretical frequency curves, the values of the main statistical indicators and the χ^2 test values for the distributions concerning the apron undermining: a) by degrees of depth of apron undermining; b) by categories of proportion of damage to the apron width; c) by degrees of global magnitude of damage

Table 6. The main results obtained with respect to the magnitude of the four researched events

Running no.	Name of damage	Characteristic studied in order to estimate the magnitude of damage	Unit of measurement	Class amplitude	Arithmetic mean	Variation coefficient (%)	Normal	Charlier-type A	Beta
1	Breakage of apron zone terminal spur	Depth of breakage	m	0.5	1.14	44.53			
		Proportion of breakage	%	20	60.00	48.15	-		
		Global magnitude of breakage	-	1	3.12	54.46	-	-	
2	Erosive damage	Depth of erosive damage	cm	5	6.98	86.47	-		-
				10	7.50	80.18	-	-	-
		Proportion of erosive damage	%	10	29.16	82.73	-		-
				20	29.58	81.90	-		
		Global magnitude of erosive damage	-	1	1.50	67.37	-		-
3	Body undermining	Depth of body undermining	m	0.5	0.81	56.01			
		Proportion of body undermining	%	20	58.00	36.39			
		Global magnitude of body undermining	-	1	2.93	37.48			
4	Apron undermining	Depth of apron undermining	m	0.5	0.93	55.18			
		Proportion of damage to the apron width	%	20	54.32	50.69			
		Global magnitude of apron undermining	-	1	2.86	55.89	-		

Note: The cells in the table rendered in grey tones represent the research characteristics of the magnitude of damages for which the concordance between the experimental and theoretical frequency was shown.

The quality of fitting (estimated by means of the value of $\chi^2_{\text{exp}}/\chi^2_{\text{theor}}$ ratio) ranks the theoretical distributions in the order: for the first characteristic, Charlier type A distribution, normal distribution and Beta distribution; for the second characteristic, Beta distribution, Charlier type A distribution and normal distribution; for the third characteristic, Beta distribution, Charlier type A distribution and normal distribution.

Consequently, regarding the magnitude of the apron undermining event, a normal frequency distribution was shown for two of the three studied characteristics.

3.5. Synthesis of the main results. Discussion

The results of the statistical approach developed from this research, represented synthetically in the Table 6, represent answers to the three scientific questions formulated in the introductory part of this paper.

The frequency distributions formed and studied in order to find these answers show that the values of the main statistical indicators and the experimental values of the χ^2 concordance test depend on: the nature of the damage, the nature of the criterion used for characterising damage magnitude, and the amplitude of the interval used for grouping frequencies into classes.

The limits of the variation coefficient vary as follows:

- between 30% and 40%, in the case of body undermining, when the studied characteristics are the proportion of body undermining and the global magnitude of body undermining;
- between 40% and 50%, in the case of the breakage of terminal spur, when the studied characteristics are depth of breakage and proportion of breakage;

- between 50% and 60%, for breakage of terminal spur when the researched characteristic is the global magnitude of breakage, for body undermining when the researched characteristic is depth of body undermining, and for apron undermining, irrespective of the nature of the studied characteristic (depth of undermining, proportion of damage to the apron width, or global magnitude of undermining);

- between 80% and 90%, for the event of erosive damage, when the researched characteristics are depth and proportion of the erosive damage (irrespective of the amplitude of class interval).

If comparative analysis is limited only to the global magnitude of events, the four types of studied damage are ranked on a scale of the variation coefficient as follows:

- body undermining, between 30% and 40%;
- breakage of terminal spur and apron undermining, between 50% and 60%;
- erosive damage, between 60% and 70%.

Consequently, in all the studied cases, the variation coefficient of the magnitude of the event exceeds the threshold of 30%, considered the limit to move from homogeneous distributions to non-homogeneous distributions (Giurgiu, 1972). Hence, it is recommended that future developments of scientific research should also take into consideration the homogenisation of the watershed statistical population, through the stratification of the structures affected by various behavioural events according to the most important factors causing the variability of the magnitude of these events.

According to the average recorded by the global magnitude of damage during the period spanning from the structures construction, three events (breakage of terminal spur, body undermining and apron undermining) were of medium intensity, and the fourth (erosive damage) was of low intensity.

For damage caused by body undermining and apron undermining, the normal frequency distribution was statistically shown for all three characteristics used in order to discover the variation laws of magnitude. For the damage concerning the breakage of the terminal spur, normal distribution was highlighted only for one of the three research characteristics that were considered whereas, for the erosive damage of structures, normal distribution could not be shown statistically for any of the three research characteristics that were used.

Charlier type A and Beta theoretical distributions showed their flexibility (also) in the case of fitting the experimental frequencies that were formed and studied, for the first time, in this paper. Indeed, the magnitude of the four events under analysis generated sequences of experimental frequencies that, in most cases, proved to be consistent with the sequences of theoretical distributions corresponding to the two aforementioned distributions. In conclusion, for the group of the four events classified as damages, normal, Charlier type A and Beta theoretical distributions can provide solutions of fitting the sequences of experimental frequencies for any of the characteristics defined with a view to estimating the magnitude of damages.

Finally, in case of performing a classification of theoretical distributions according to the number of experimental distributions that the first fit, it can be noted that Charlier type A distribution holds the first position with 12 fitted distributions (out of a total of 15), while Beta distribution, with 10 fitted experimental distributions, holds the second place. In this classification, the normal distribution occupies the third place, providing solutions for 6 out of the 15 studied experimental distributions.

4. Conclusions

This paper's findings are most applicable to future scientific research; nevertheless, they also have practical significance.

The magnitude of damage patterns – as a random variable the knowledge of which is essential in order to conceive and to apply a programme of systematic and permanent monitoring of the hydrotechnical torrent control structures – has to be quantified, for each event separately, both by means of two statistical indicators (arithmetic mean and variation coefficient) and in the form of a theoretical function, that can be used to predict the frequency of behavioural events, by different degrees of intensity, over the entire functional period of the structures.

Knowing frequency distributions does not have only a theoretical value, but also has a practical value. Indeed in managed torrential watersheds, similar to those taken in study, where detailed research can be done, there are possible estimations of the number of structures that can be affected with a certain intensity of events. In this way an

anticipated planning of funds is possible for a rehabilitation programme.

As well as this, for organising the research regarding damage patterns, the variation coefficient provides an important practical factor. This coefficient can be useful in research for establishing the number of structures taken into consideration for a certain degree of precision.

The practical value of the results emerges from the fact that the intensity of each event taken into consideration is reflected, with a certain weight, in the physical status of the structure. If this weight is established (using a multicriterial analysis) and if summing the products between intensity and weight of events during the functioning period of the structures then a so called “structure condition index” can be defined.

Taking this index into consideration, the structures can be classified (such as having a very bad, bad, medium, good or very good structural condition) and prioritised for accomplishing necessary rehabilitation operations.

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ELECTROMAGNETIC POLLUTION OF THE HOSPITAL ENVIRONMENT DUE TO NEW GENERATION MOBILE PHONES

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Abstract

The aim of this paper is to characterize the electromagnetic pollution of the hospital environment and to determine what effects it could have on patient care, focusing on the electromagnetic interference phenomena of medical devices due to new generation mobile phones emissions. Measurements results of the electromagnetic background and mobile phone emissions are presented, along with the effects on specific susceptible medical devices.

Key words: electromagnetic interference, hospital environment, mobile phones

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1. Introduction

Mobile phone technology has proven its efficiency in data exchange and ease of use (Laurer et al., 2008) and is now the most widespread means of communication worldwide. Wireless communications contribute to this environment pollution, the electromagnetic interference risk to medical equipment it poses and the human exposure (Lunca et al., 2012; Morega et al., 2011) made the object of numerous studies worldwide.

The electromagnetic interference phenomenon leads to incorrect recordings of biological signals and, subsequently could lead to an incorrect diagnosis if it is not identified, like in the case of electrocardiograms (Baranchuk et al., 2009).

Medical equipment used in hospitals comply with the IEC EN 60601-1-2 standard regarding electromagnetic compatibility that imposes life supporting equipment to be immune to a maximum

electric field of 10 V/m and a 3 V/m immunity for non life supporting medical equipment. The problem is that these maximum field values could be exceeded in some cases.

Taking into consideration the fact that medical devices are exposed to various electromagnetic fields and that their malfunction due to electromagnetic interference could pose a serious risk to the patient or the medical personnel, a rigorous characterization of this environment is required, determining the field sources and possible susceptible medical equipment.

Although it was suggested that mobile phones should not be used in hospitals (Helhel et al., 2011), or that they can be used maintaining a safe distance from medical equipment (Cohen et al., 2005; Small, 2005), the fact remains that wireless technology is a part of the medical service and, taking into consideration technological advancement, the hospital electromagnetic environment tends to be

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increasingly populated by these emissions in the future.

By far, the most common wireless technologies used in hospitals are GSM/ E-GSM (800-960 MHz), DCS (1710-1880 MHz), 3G (1920-2180 MHz), Wi-Fi (2.4 GHz), UMTS (1.8-2 GHz, 2.1-2.2 GHz) and the two way radio stations used by the ambulances (25-50 MHz). Other wireless technologies present in the hospital environment are EN301- implantable (9–315 kHz), RFID-personal body network (125–134.2 kHz, 13.56 MHz, 868–954 MHz), Bluetooth and the IEEE 802.15.1 standard (2.4-2.5 GHz), Zigbee (2.4 GHz, 902 MHz (US), 68 MHz (EU), 802.11, 802.11a, 802.11b, 802.11g, 802.11n, 802.11p, 802.11s (2.4- 5.9 GHz), IrDA (1-430 THz), 802.20 (1.25 or 5 MHz) (Dafinescu et al., 2010; Grant et al., 2001; Iskra et al., 2007; Lauer et al., 2008; Rashvand et al., 2008; Ziegelberger et al., 2008).

Mobile phones using are the most likely source of electromagnetic fields that can come in close proximity, or even in contact, with medical equipment, having a maximum antenna output power (radiating power) between 125 mW and 2 W and a maximum antenna output power for Wi-Fi connection of 100 mW. A consequence of the electromagnetic pollution of the medical environment is the malfunction of medical devices as a result of electromagnetic interference. An electronic medical device can act in this environment as a source of pollution, as a victim or as both at the same time (Dafinescu et al., 2006, 2011).

Each medical device will respond to the electromagnetic field in a certain way, by a function of it's orientation and distance from the emitting source, the number and complexity of the device's components, it's construction (shielding, openings in the case), operating frequency and accessories (sensors, electrodes, cables) (Coll et al., 2010; LaSorte et al., 2009, 2010; Riederer et al., 2010; Vlach et al., 1995).

2. Experimental

In order to determine the electromagnetic emissions that are present in the hospital, a mobile phone was selected for testing. This selection was made based on an estimation of the phone model's popularity on the market and on its communication functions. Because the emissions of mobile phones depend on the distance between the device and the network provider's base station, we chose to use three subscriber identification modules (SIM), from the most popular networks being used by patients and doctors alike, to conduct the tests.

For the characterization of electromagnetic pollution to the environment, a series of measurement tools were used, mainly a spectrum analyzer ROHDE & SCHWARZ FS300 with a frequency range of 9 KHz - 3 GHz and a horn antenna (model AT4002A) with a frequency range of 0.8-5 GHz. The measurements were made in the 0.8-

3 GHz frequency range in order to characterize the emissions of mobile phones, compared to the electromagnetic background. All measurements were made with the mobile phone in normal use, in order to emulate real life conditions. The „Max Hold” mode setting to the spectrum analyzer was used in order to analyze “the worst case scenario”, to determine the maximum electric field emitted by mobile phones and the corresponding frequency (David et al., 2009). The spectrum analyzer was connected to a portable computer for data storage and analysis, all measurements results being stored for future processing. For all the measurements made, the antenna factor F_a was calculated using the antenna gain G (David et al., 2009), and the electric field was determined using Eq. (1).

$$E[V/m] = 10^{\frac{E[dB\mu V/m]}{20}} \cdot 10^{-6} \quad (1)$$

$$E[dB\mu V/m] = U_E[dB\mu V] + F_a[dB] + C_l[dB] \quad (2)$$

$$F_a[dB] = 20 \lg \frac{9.73}{\lambda \sqrt{G}} \quad (3)$$

$$U_E[dB\mu V] = P[dBm] + 107 \quad (4)$$

based on Eq. (2), Eq. (3) and Eq. (4), where U_E is the voltage at the antenna terminals, P is the measured power, λ is the wavelength and C_l is the cable loss.

3. Results and discussion

In this section the electromagnetic pollution of the environment from a qualitative and quantitative point of view is presented, highlighting the consequence of this pollution in the hospital environment, focusing on the malfunction of electronic medical devices. An 800 MHz – 3 GHz background electric field measurement in the hospital is presented in Fig. 1, showing the contributions of wireless technology in the electromagnetic pollution of this environment. These results were taken in the course of 12 hours, representing the average of 12 different measurements, 10 minutes each, using the “Max Hold” function of a spectrum analyzer.

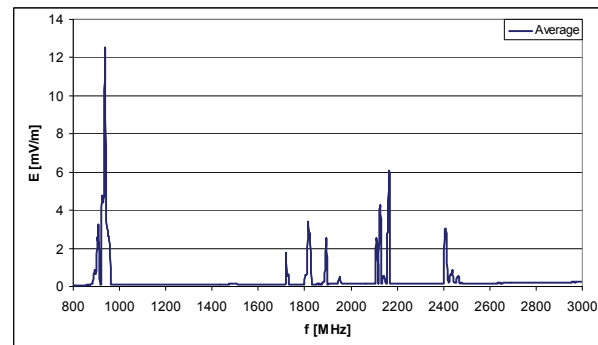


Fig. 1. Background electric field in the 800 MHz – 3 GHz frequency band

In this manner, we determined the field intensities and we identified the principal sources of electromagnetic field in the hospital and the corresponding field frequencies. A statistical processing of these background electric field measurements is presented in Table 1, where σ is the standard deviation.

Table 1. Electric field values and standard deviation for the background electric field

f [MHz]	938	1815	1893	2126	2164	2409
E_{min} [mV/m]	8.84	1.65	1.39	2.51	3.57	2.25
E_{max} [mV/m]	17.24	5.93	3.84	6.61	8.67	3.79
E_{ave} [mV/m]	12.47	3.35	2.54	4.27	6.06	3.03
σ [mV/m]	2.73	1.34	0.76	1.54	1.3	0.51

The use of new generation mobile phones gives way to a broader bandwidth occupation, these new models having additional functions like internet connection, this function being used in some medical applications by doctors and patients, for example in telemedicine. After the assessment of the electromagnetic environment and a number of tests, we decided to focus on the GSM and Wi-Fi emissions of a new generation mobile phone.

3.1. Characterization of mobile phones emissions

A very important part in determining electromagnetic field interference cases is the characterization of the field sources that could be responsible for this phenomenon. In this view, the emissions from mobile phones are analyzed and the results are presented in this section.

3.1.1. GSM

In the following, the measurements results of the maximum values measured, in the frequency range of 880 – 960 MHz, covering the E-GSM 900 and the P-GSM 900 bands are presented.

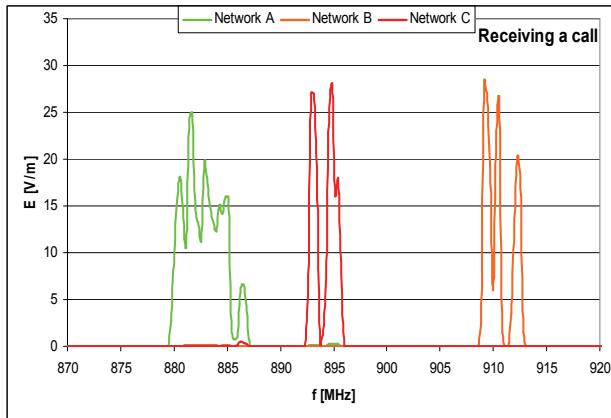


Fig. 2. Maximum values of E at 10 cm from the mobile phone when receiving a call

The emitted fields were measured while the phone was making or receiving a call because, in the first case, the maximum emitted field was observed when the link was made from the mobile phone to the base station of the network provider, and the case of receiving a call is an unknown factor to the user, and it can happen anytime. This last case is the most important in the interference phenomena with medical devices. The maximum values of the electric field while receiving and making a call, using the same mobile phone model, connected to the three different networks, measured with the horn antenna at 10 cm from the phone, are shown in Fig. 2 and Fig. 3, respectively.

The decrease of the electric field with the increase of distance from the phone and the corresponding frequencies are shown in Table 2, for the cases of receiving and making a call, respectively. Only the maximum values of the electric field were taken into consideration. Measurements of the electric field generated by the mobile phone were also performed using a RFP-04CE smart field meter and an isotropic electric field probe PI-01 with a frequency bandwidth of 0.2 MHz ÷ 3 GHz, being able to measure an electric field up to 600 V/m.

Measurements results were comparable with the ones obtained by using the spectrum analyzer and the horn antenna, as can be seen in Table 3. The difference between the electric field values obtained in the same conditions but with the two different measurement setups were below 20 %. For distances above 1 m the electric field measured using the RFP-04CE field meter varied due to the emissions caused by other sources because of the wide bandwidth of measurement. The electric field emitted by the mobile phone in all the scenarios that were considered was higher than the electromagnetic field immunity limits imposed by standards for medical equipments of 3 V/m up to a distance of 2 m, making the mobile phone a possible source of electromagnetic fields that could lead to electromagnetic interference phenomena of medical equipment.

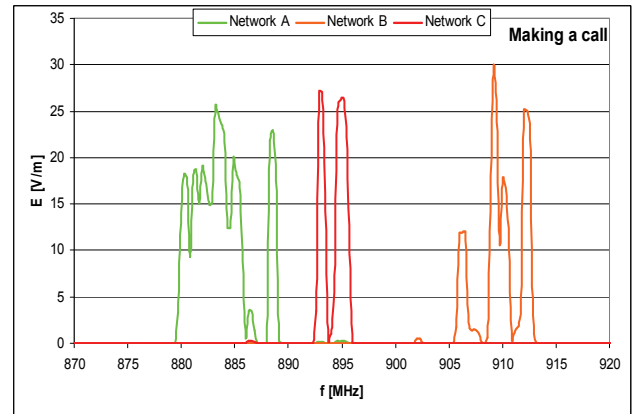


Fig. 3. Maximum values of E at 10 cm from the mobile phone when making a call

Table 2. Maximum values of the electric field at some distances from the mobile phone

Distance [cm]	NETWORK A				NETWORK B				NETWORK C			
	Making call		Receiving call		Making call		Receiving call		Making call		Receiving call	
	Frequency [MHz]	E [V/m]	Frequency [MHz]	E [V/m]	Frequency [MHz]	E [V/m]	Frequency [MHz]	E [V/m]	Frequency [MHz]	E [V/m]	Frequency [MHz]	E [V/m]
10	883.1	25.6	882.2	24.99	909.1	29.77	909.1	28.43	892.8	27.02	894.8	28.01
50	882	8.18	888.5	10.35	909.4	11.45	909.1	12.26	895.4	10.77	895.4	12.09
100	886.2	7.66	882	7.12	909.1	7.47	909.1	7.39	894.5	6.87	894.5	6.56
200	886.5	3.62	888.5	3.59	912.2	4.07	912	3.93	894.8	3.56	893.1	3.4
300	888.5	1.58	886.5	1.67	912.2	1.39	910.2	2.13	895.4	1.42	895.4	1.47

Table 3. Maximum electric field measured with the RFP-04CE field meter

Distance [cm]	NETWORK A		NETWORK B		NETWORK C	
	Making call	Receiving call	Making call	Receiving call	Making call	Receiving call
	E [V/m]	E [V/m]	E [V/m]	E [V/m]	E [V/m]	E [V/m]
10	23.83	22.7	30.64	30.5	31.3	31.02
50	8.64	9.28	11.3	11.4	9.52	12.88
100	8.28	8.3	8.2	7.66	8.11	7.9

3.1.2. Internet use

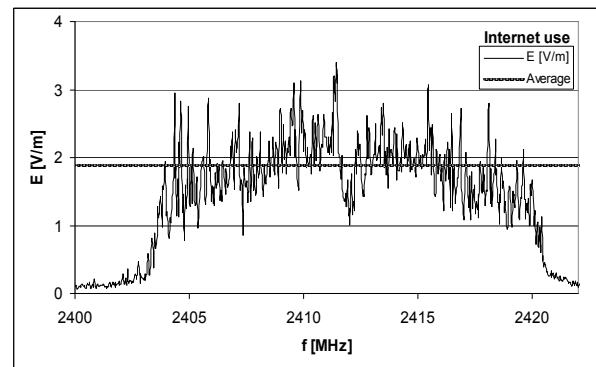
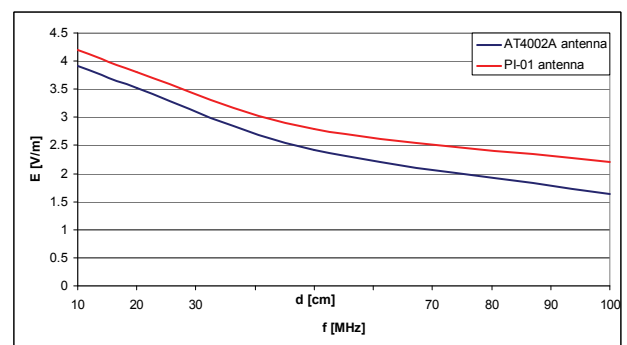
In order to determine the emissions of the mobile phone due to IEEE 802.11 Wireless LAN connection, we measured the electric field in the 2.3 – 2.5 GHz frequency band, at a distance from the mobile phone from 10 cm to 1 m. Results obtained for measurements made at a distance greater than 1 m showed an electric field smaller in amplitude than 1.5 V/m, and are not presented in this paper.

A trace of the electric field measured at 20 cm distance from the mobile phone while surfing the internet, downloading and uploading files, is shown in Fig. 4. It is clear that the electric field generated by the mobile phone in this operating mode can exceed the 3 V/m immunity level for non-life supporting medical devices. An average value of the measured electric field however is lower than this level and this operating mode shouldn't affect the normal functioning of a medical device.

In Fig. 5, the decrease of the electric field due to internet use on the mobile phone is shown, in respect to the distance from the emitting source, comparing the results obtained using the horn antenna and the spectrum analyzer with the results obtained with the RFP-04CE field meter and the PI-01 antenna and a good correlation between the results can be observed. The maximum electric field measured in the case of internet use on the mobile phone at a distance of 10 cm to the measuring horn antenna was 3.91 V/m, corresponding to a frequency of 2411 MHz.

Using the spectrum analyzer in “Max Hold” mode, although not suited for characterizing these kind of digital signals, allowed us to determine if the mobile phone could be a possible threat to medical devices while using the internet. The probability of electromagnetic interference to medical equipment

due to the emissions of the mobile phone in this operating mode is very low, especially taking into account the fact that surfing the internet on the mobile phone is a voluntary act, and could be prevented by electromagnetic compatibility awareness among medical staff and patients, contrary to the case of receiving a call.

**Fig. 4.** Electric field at 20 cm from the mobile phone when using the internet**Fig. 5.** The electric field emitted by the mobile phone while using the internet, versus distance

3.2. Medical equipment electromagnetic interference due to mobile phones

In the case of interference due to mobile phone emissions, the risk rises because the distance of the source in respect to the victim depends on the phone's owner and in the worst cases, the medical device and the phone could be in direct contact. The effects of the electromagnetic fields on medical equipment could be transitory or permanent, some of these being discussed in Dafinescu et al. (2010, 2011). A specifically susceptible class of medical devices is that of devices used for monitoring biological signals like electrocardiographs (EKG), encephalographs (EEG) or electromyography devices (EMG). A case of interference due to GSM emissions is presented in Fig. 6, when the mobile phone was ringing at a distance of 10 cm from an EEG electrodes input box. The sensitivity of the EEG was set at $150 \mu\text{V}/\text{cm}$. No interference was observed to the device when the distance of the phone was greater than 1 m.

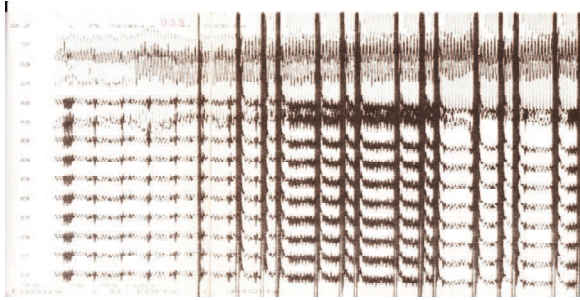


Fig. 6. Interference due to GSM emissions on the EEG

In Fig. 7 (a), a mobile phone's ringing effect at a distance smaller than 10 cm from an EKG patient monitor can be seen, in respect to a normal EKG recording, Fig. 7 (b), when no interference was observed (distance greater than 10 cm).

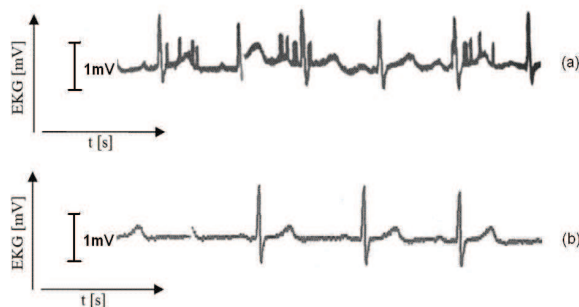


Fig. 7. EKG recording: (a) with interference due to mobile phone, (b) normal

This kind of malfunction of medical devices could make patient care very difficult for doctors and is an unacceptable phenomenon when diagnosing, treating or monitoring a patient. This is why the sources of such undesired events have to be studied in view to minimize and control further malfunction of medical equipment.

In order to better characterize the influence of mobile phone emissions on the measurement of EKG, EEG and EMG signals, we used a BIOPAC measurement setup and used a mobile phone in the vicinity of the electrodes. The amplifier of the EKG module was set to a gain of 1000 and a call was received (without answering) on the mobile phone placed at 0.5 cm from the electrode on the right hand. The effect on the EKG recording can be seen in Fig. 8, after the 4th second. A 6.2 V peak to peak noise is overlapping the normal EKG recording, making it unreadable. Similar effects were determined while placing the mobile phone near the left hand and right foot electrode (Einthoven configuration).

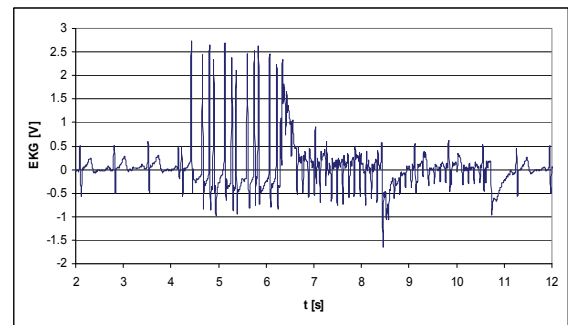


Fig. 8. EKG recording with interference while receiving a call at 0.5 cm from the right arm electrode

These effects ceased when the distance between the mobile phone and the electrodes was greater than 10 cm. Using an EEG acquisition module of the BIOPAC we tested the interference due to mobile phone ringing using 3 electrodes and the effects on the EEG recording for a distance of 1 cm from the electrodes is presented in Fig. 9 where a 4.07 V peak to peak noise is disrupting the normal EEG signal measured with a 5000 gain amplifier. In this case, the interference ceased after placing the mobile phone at a distance greater than 1 m.

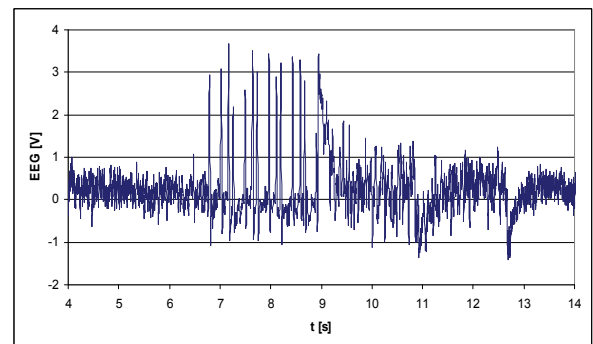


Fig. 9. EEG recording with interference while receiving a call at 1 cm from the electrode

Electromagnetic interference phenomenon awareness in the hospital would greatly minimize the malfunction of medical devices and reduce the risk to patients and medical personnel alike. Also, knowing the possible sources of electromagnetic fields and

how they pollute this environment gives way to regulations about their use and safety distances from possible victims.

4. Conclusions

A characterization of the electric fields in the hospital environment due to wireless communication systems and their effects on some medical devices is presented in this paper. A statistical processing of a 12 hours electromagnetic background survey, for the 0.8 – 3 GHz frequency band showed that the maximum field levels did not exceed 20 mV/m.

The emissions due to new generation mobile phones were characterized taking into consideration 3 different network providers and different distances from the mobile phone while receiving and making a call and while using the internet, the maximum electric fields generated by mobile phone being greater in some cases than the immunity standard levels for medical electronic equipment.

A study on the electromagnetic interference of EEG and EKG devices due to GSM emissions from a new generation mobile phone was made, revealing that the acquisition of biological signals is perturbed at distances less than 1 m between the mobile phone and the medical device.

Based on the electric field emitted by the mobile phones presented in this paper and the electromagnetic interference cases studied, a safe distance between medical equipment and mobile phones of at least 1 m should be kept in order to avoid these phenomena. Taking into consideration the advantages of using mobile phones, a ban of these devices from the medical environment is unfeasible at best.

Acknowledgements

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ELUCIDATING CHARACTERISTICS OF GEOPOLYMER WITH SOLAR PANEL WASTE GLASS

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Abstract

This study examined the characteristics of geopolymer with solar panel waste glass. After 28 days of curing, the compressive strengths of the geopolymer samples containing 10 mass % and 20 mass % solar panel waste glass were 63.3 ± 1.8 and 49.1 ± 2.2 MPa, respectively. The geopolymer sample with 10% solar panel waste glass exhibited a stronger reaction than that with 20% solar panel waste glass, and the strength decreased as the amount of solar panel waste glass increased. Thermo-gravimetric and differential thermal analysis (TG/DTA) results showed that the mass loss of geopolymer after heating declined as the amount of solar panel waste glass increased. The principal peaks in the Fourier transformation infrared spectroscopy (FTIR) spectra correspond to the Si-O-Al bond in geopolymer. Scanning electron microscopy (SEM) observations indicated that the microstructures of the stronger samples were more homogeneous, and the microstructures of geopolymer with 10% solar panel waste glass did not exhibit substantial deterioration. The experimental results indicate that solar panel waste glass has the potential to serve as a partial replacement of metakaolinite and exhibits favorable mechanic characteristics.

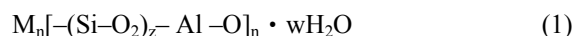
Key words: alkali-activated, compressive strength, geopolymer, metakaolinite, solar panel waste glass

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1. Introduction

Geopolymer is new class of building materials that is widely used worldwide in recent years. It is a type of three-dimensional aluminosilicate binder, which was developed by Davidovits (1991). It is the product of the reaction of solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution. In a strongly alkaline solution, aluminosilicate is rapidly dissolved to form free SiO_4 and AlO_4 tetrahedral units. As the reaction proceeds, SiO_4 and AlO_4 tetrahedral units are linked by oxygen atoms to yield polymeric Si-O-Al bonds, the empirical chemical formula of which is shown in (Eq. 1), where M is an alkali metal cation, such as

potassium and sodium, and n represents the degree of polycondensation; z is 1, 2, 3 (Khale and Chaudhary, 2007).



Geopolymer is an aluminosilicate material with several properties, including effective acid and fire resistance, compressive strength, durability, and an ability to immobilize toxic and radioactive materials (Duxson et al., 2007a; Komnitsas and Zaharaki, 2007; Palomo et al., 1999; Temuujin et al., 2009). Interest in geopolymer has increased in recent years because of its wide range of potential applications in civil engineering and several other

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industrial sectors (Andini et al., 2008; Rovnanik, 2010; Temuujin et al., 2009).

In recent decades, the reuse and recycling of industrial solid wastes and municipal solid wastes have attracted substantial interest in Taiwan (Chiang et al., 2010; Chow et al., 2008; Ghosh and Ghosh, 2013; Lin et al., 2009, 2011; Popovici et al., 2013). According to Taiwan's Environmental Protection Administration (EPA), 0.75 million tons of garbage was disposed in 2006, 5.84% of which was waste glass (Lin, 2007). The cumulative amount of waste glass that was dumped into landfills in Taiwan is approximately 0.52 million tons, whereas the amount of solar panel waste glass has reached 1000 tons. A solar panel includes crystalline silicon and a thin film. The most established thin film solar panel technology is based on amorphous silica (a-Si).

The demand for solar panels will increase the amount of produced solar panel waste glass. The conventional treatment of solar panel waste glass involves the landfill process; however, landfilling is not a favorable option because it imposes a considerable financial burden on foundries (Liao, 2009) and makes them liable for future environmental costs and problems, as required by the landfill regulations.

Solar panel waste glass comprises mainly SiO_2 and can be used to prepare geopolymer. This study examined the characteristics of geopolymer that contains solar panel waste glass. The results of this study will contribute to the promotion of solar panel waste glass recycling technologies to help to achieve the goal of sustainable development and establish a recycling society with zero discharge.

2. Materials and methods

2.1. Materials

The geopolymer was synthesized from metakaolinite, which was prepared by calcining kaolinite from Pei-Long Enterprise CO., LTD. in Taiwan at 650°C for 3 h. Solar panel waste glass was collected from a solar panel manufacturing plant in Taiwan. The main constituents of raw materials were showed in previous study (Gao et al., 2014). The solar panel waste glass was ground to a Blaine fineness value of approximately $360 \text{ m}^2 \text{ kg}^{-1}$. The resultant pulverized solar panel waste glass was desiccated before being tested.

2.2. Experimental procedure

NaOH and sodium silicate solution were mixed using an electrical mixer for five minutes and cooled to room temperature. Then, the activator was added to the metakaolinite and the powdered solar panel waste glass, and stirred for another ten minutes. The homogenous slurry was then poured into cubic plastic moulds with a volume of $50 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$.

Samples were cured in a laboratory oven at 30°C and an ambient pressure for 24 h before they were removed from the moulds. Experiments were carried out on the mechanical strength of the samples after the specified number of days of curing.

2.3. Blend ratios of the geopolymer paste samples

Table 1 presents the blend ratios of the geopolymer paste samples. The effects of solid/liquid (S/L, powder of metakaolin and solar panel waste glass to alkali solution ratio), $\text{SiO}_2/\text{Na}_2\text{O}$ (Ms, the alkali solution contained molar of SiO_2 to Na_2O ratio) on the strength of the geopolymer pastes were examined. Based on the results of the two experiments, the effects of the ratios S/L and Ms on geopolymer with solar panel waste glass were examined.

Table 1. The blend ratios of the geopolymer paste samples

Series	Blend ratios of samples		Samples proportion by weight percent (wt %)		
	S/L*	Ms**	Kaolinite	Na_2SiO_3	NaOH (10 M)
S/C	1.0	1.0	50	26.1	23.9
	0.8	1.0	44.4	29.0	26.6
	0.6	1.0	37.5	32.6	29.9
	0.4	1.0	28.6	37.3	34.1
S/N	0.8	0.75	44.4	23.7	31.9
	0.8	1.00	44.4	29.0	26.6
	0.8	1.25	44.4	33.6	22.0
	0.8	1.50	44.4	37.5	18.1
	0.8	1.75	44.4	40.9	14.7

2.4. Analytical methods

The following major analyses of the geopolymers with and without solar panel waste glass were performed.

(1) Compressive strength tests were performed after 1, 7, 14 and 28 days using a $50 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$ cubic sample, according to ASTM C109.

(2) Chemical composition: The samples were tested by an automated RIX 2000 spectrometer.

(3) Mineralogy: The samples were characterized by X-ray diffraction (XRD) using the $\text{CuK}\alpha$ radiation on a Siemens D-5000 X-ray diffractometer 2 θ scanning, ranging between 10° and 80° and the XRD scans were run at 0.05° -increments, with a 1 sec counting time.

(4) Fourier transformation infrared spectroscopy (FTIR) was carried out on samples using a Bomem DA8.3 spectrometer.

(5) Scanning electron microscopy (SEM): the microstructure of the geopolymer was observed using a Hitachi S-3500N.

(6) Differential Thermal and Thermo-gravimetric Analysis (DTA/TGA): DTA/TGA analysis was done on a Seiko SSC Model 5000 Thermal Analyzer at $25^\circ\text{C} / \text{min}$ heating rate in the 25°C - 1000°C temperature range.

3. Results and discussion

3.1. Characteristics of raw materials

The main components of solar panel waste glass were amorphous, as revealed by their broad diffuse bands. The main crystalline component identified in kaolinite is quartz and $(\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4)$. During the transition from kaolinite to metakaolinite, the kaolinite structure disappeared and was amorphous. XRD patterns of raw materials are presented in the work of Hao et al. (2013).

Fig. 1 presents the FTIR spectra of the raw materials. The peaks of waste glass around 470 cm^{-1} , 1008 cm^{-1} , 1031 cm^{-1} and 1087 cm^{-1} correspond to the asymmetric stretching of Si-O-Si. Kaolinite presented the asymmetric stretching of Si-O-Si around 470 cm^{-1} , 540 cm^{-1} , 880 cm^{-1} and $950\text{--}1200\text{ cm}^{-1}$, which were attributed to Si-O-Si bending, the octahedral of Si-O-Al, asymmetric stretching of Si-O-Si and the asymmetric stretching of T-O-Si (T: Si or Al), respectively. The bands around 917 cm^{-1} was related to the OH bending. The peaks around 3640 cm^{-1} and 1680 cm^{-1} correspond to the bending vibration of HOH. The peaks of metakaolinite around $950\text{--}1200\text{ cm}^{-1}$ related to T-O-Si.

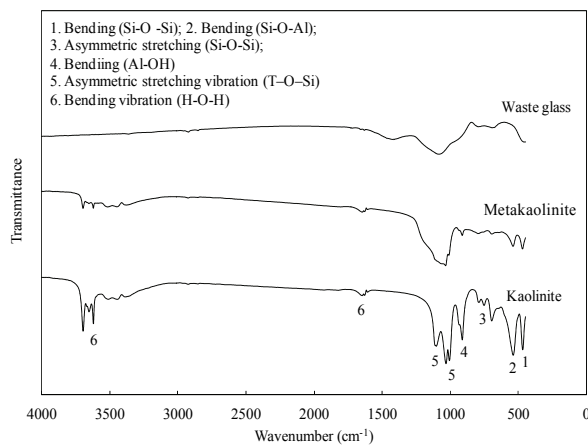


Fig. 1. FTIR spectra of raw materials

3.2. Compressive strength of geopolymer without solar panel waste glass

Fig. 2 shows the compressive strength of the S/C series from Table 1 as a function of S/L (S/L: powder of metakaolin and solar panel waste glass to alkali solution ratio). The compressive strength increased in conjunction with S/L for a specific curing time. The compressive strength of the geopolymer increased as curing time (except for S/L = 0.6 and S/L = 0.4 at 28 days). The strength increased rapidly after the first 24 hours, and subsequently increased slowly. The relationship between silica and alumina in the metakaolin-based geopolymer system is responsible for the increase in strength (Somna et al., 2011). The compressive strength of geopolymer at an S/L of 0.6 or 0.4 decreased after 14 days, because the geopolymer

contained excess water at a low S/L. At 1-day and 28-days, the strength of the geopolymer with an S/L of 0.8 was 42.12 and 48.34 MPa, respectively (slightly lower than for the geopolymer with an S/L of 1.0); when the S/L was 1.0, the mixtures were sticky and difficult to pour into the mold. Therefore, from a practical point of view, the optimal S/L was 0.8.

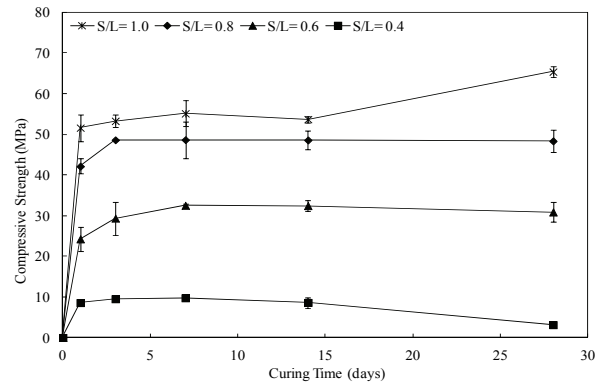


Fig. 2. Compressive strength of geopolymer without glass for various S/L

Fig. 3 shows the results of the compressive strength tests on the S/N series, and Table 1 shows various Ms ratios.

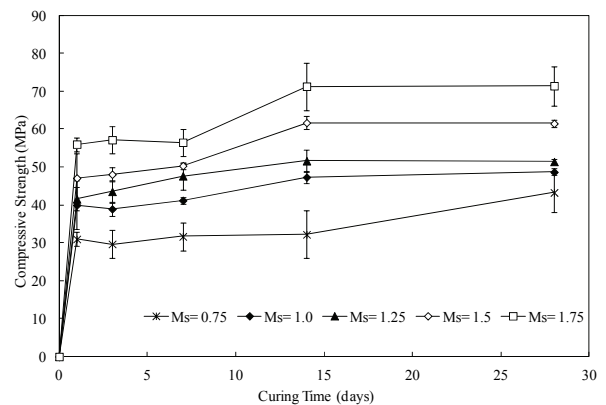


Fig. 3. Compressive strength of geopolymer without glass for various Ms

The effect of Ms on the strength was similar to that of S/C series, and increased in conjunction with curing time. The compressive strength of the geopolymer increased in conjunction with Ms. The increase in the strength of the geopolymer in conjunction with the silica content may have occurred because Si-O-Si bonds are stronger than Si-O-Al bonds (Duxson et al., 2005). The graph shows that the strength of geopolymer with an Ms of 1.75 was 56.02 MPa at 1-day and 71.42 MPa at 28-days. The results indicate that geopolymer with a higher Ms had a higher compressive strength. Therefore, the optimal Ms was 1.75.

3.3. Compressive strength of geopolymers with and without solar panel waste glass

Fig. 4 shows the compressive strength of the geopolymer with solar panel waste glass for S/L 0.8

and Ms 1.75. The compressive strength increased in conjunction with curing time, and decreased as the solar panel waste glass content increased. At 28 days of curing, the compressive strength of the geopolymer with 10% solar panel waste glass was 63.27 MPa, which was 88.2% that of pure metakaolinite geopolymer, and the compressive strength of the geopolymer with 20% solar panel waste glass was 49.06 MPa.

The compressive strength decreased as the amount of solar panel waste glass increased, because the excess solar panel waste glass, which supplied the silica, reduced the aluminum that was in metakaolinite; therefore, it was more difficult to synthesize the aluminosilicate. Therefore, the optimal amount of waste glass in the geopolymer was 10%, which demonstrated the use of waste glass in the geopolymer mixture by partial substitution of costly metakaolinite with the cheaper waste glass without considerable deterioration of the geopolymer.

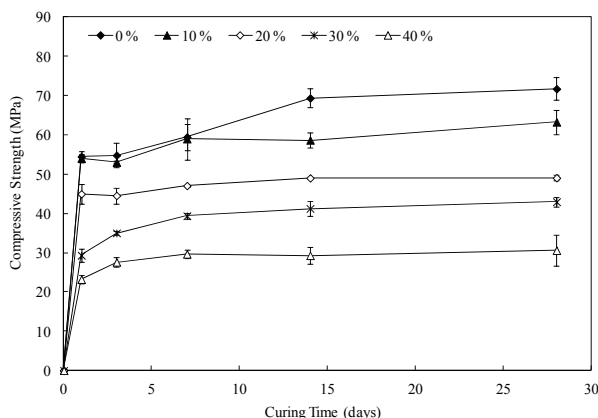


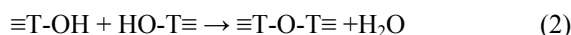
Fig. 4. Compressive strength of geopolymer with solar panel waste glass

3.4. Differential thermal and thermogravimetric analyses of geopolymers with and without solar panel waste glass

Water is a crucial structural component of a geopolymer. The loss of mass of a geopolymer may be attributed to the evaporation of absorbed and bonded water. The absorbed water is lost at temperatures less than 100°C; increase of temperature results in shrinkage and damages the geopolymer structure (Daniel et al., 2008). The remaining water is either bound tightly or is less able to diffuse to the surface and continues to evaporate slowly at higher temperatures (Riessen, 2007). The continuous weight loss up to almost 500 °C is caused by the evaporation of hygroscopic water or water residing in the channels (Perraki et al., 2005).

TG/DTA was used to determine the mass loss of the geopolymer with solar panel waste glass for S/L 0.8 and Ms 1.75. Fig. 5 shows the DTA curves of geopolymer with solar panel waste glass after 28 days of curing. An endothermic peak of the DTA curve was observed at approximately 100- 400°C, revealing an obvious mass loss. This peak was mainly associated with the evaporation of free pore

water (Duxson et al., 2006). The second endothermic peak appeared from 480 to 600°C; the endothermic peak can be caused by the elimination of water by condensation of silanol or aluminol groups on the surface of the geopolymeric gel. Eq. 2 shows the exothermic reaction, where T is either Al or Si (Duxson et al., 2007b). No apparent mass loss of metakaolinite geopolymer was observed from 650 to 770°C.



The TG of the geopolymer with solar panel waste glass followed a similar trend to that of pure metakaolinite geopolymer. When the amount of waste glass reached 40%, the endothermic peaks at approximately 600°C and 770°C, associated with the condensation of silanol and aluminol groups of the gel, were more obvious than those of other geopolymers, because the geopolymer with 40% waste glass comprised gel and unreacted waste glass, which does not yield an endothermic peak at the relevant temperature. Therefore, the endothermic peak is more obvious than that obtained from any other geopolymer, the signals from which may be disturbed by the unreacted metakaolinite. Geopolymers with 30 and 40% of waste glass, the third endothermic peak appeared from 650 to 770°C. It was the nucleation temperature of waste glass (Tulyaganov et al., 2002), because the geopolymer with 30 and 40% waste glass comprised unreacted waste glass.

Fig. 6 shows the loss of mass of geopolymer at various temperatures. The loss of mass of the geopolymer with solar panel waste glass at approximately 100- 400°C and 480- 600°C exceeded that at 650- 770°C. The results are consistent with several studies, which observed lower loss of mass at higher temperatures (Duxson et al., 2006).

At 28 days, the mass losses at 100-400°C of the pure metakaolinite geopolymer and the geopolymers with 10% and 40% waste glass were 17.75%, 19.75%, 19.36%, respectively. After heating to 480-600°C and 650-770°C, the mass loss of the geopolymer with 40% waste glass was 6.09% and 1.67%. At a specific curing time, the mass loss by the evaporation of free pore water and condensation of silanol or aluminol groups in the gel for the geopolymer indicated that the mass loss can be reduced by increasing the amount of waste glass. This observation is consistent with the development of compressive strength.

3.5. FTIR spectra of geopolymers with and without solar panel waste glass

Fig. 7 shows the FTIR spectra of the geopolymers that contained solar panel waste glass for S/L 0.8 and Ms 1.75. Table 2 shows the absorption peak of the geopolymer after curing for 28 days. Table 2 shows the peaks around 3420 cm⁻¹ and 1680 cm⁻¹ in the FTIR spectrum of the geopolymer

are associated with the adsorbed water that remained in the geopolymer sample after polycondensation. Fig. 7 shows the peaks around 1033 and 1009 cm^{-1} correspond to the individual tetrahedra asymmetric stretching of Al–O and Si–O bonds. However there is a slight shifting of 1008 cm^{-1} peak towards higher wave-numbers which might be the result of the formation of a structure at which the SiO_4^{4-} groups are replaced by AlO_4^{3-} groups as network formers. These bonds exhibited higher wavenumbers than raw materials, which indicated that the bonding structures changed in individual tetrahedral (Van Jaarsveld et al., 2002). The peaks around 810 and 539 cm^{-1} were associated with the Si–O–Al vibration of the

geopolymer, indicating that the principal peaks were associated with the Si–O–Al bond in the geopolymer following geopolymerization (Barbosa et al., 2000; Van Jaarsveld et al., 2002).

During alkali activation of metakaolinite, major disruption of the Al environment is indicated by the loss of the Si–O–Al band at 810 cm^{-1} which is replaced by several weaker bands in the range 600–800 cm^{-1} (Barbosa et al., 2000). The study results (Table 2) confirm the loss of the Si–O–Al band at 811 cm^{-1} . The band at 467 cm^{-1} is attributed to Si–O flexural vibration (Wang et al., 2005). The band around 917 cm^{-1} was related to the Al–O–Si bond.

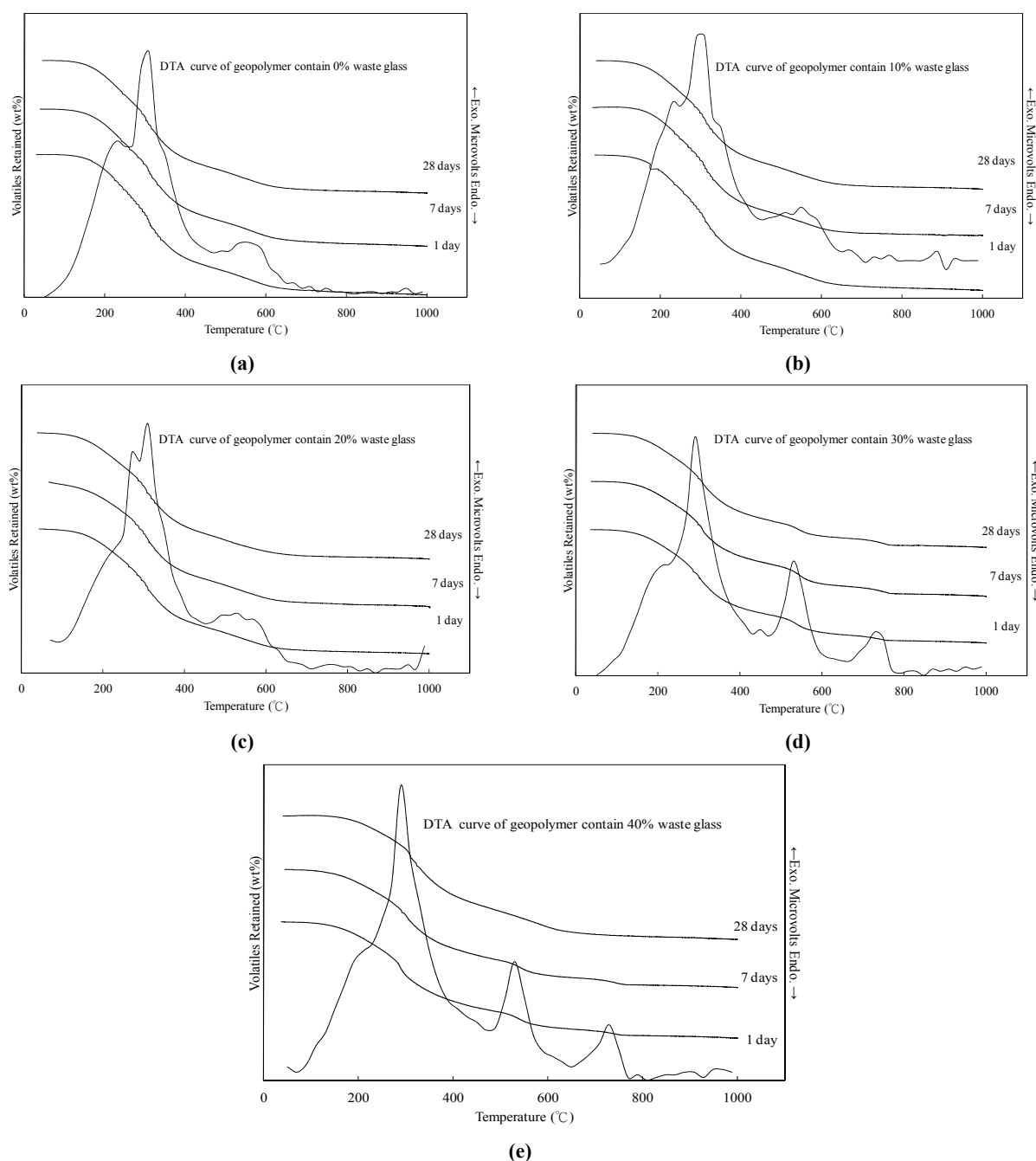


Fig. 5. TG/DTA curves of geopolymers with and without solar panel waste glass(a) 0%, (b) 10%, (c) 20%, (d)30%, (e) 40%

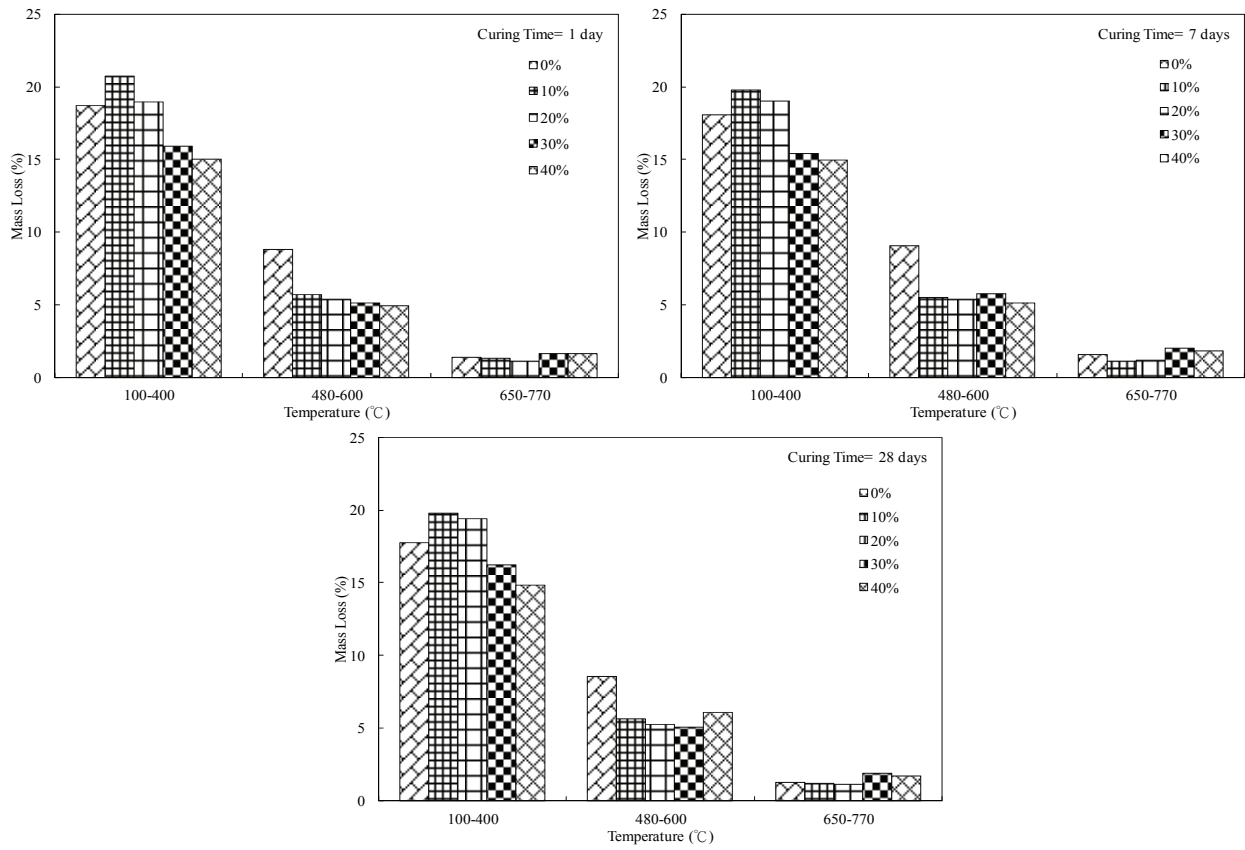


Fig. 6. Mass loss of geopolymer with and without solar panel waste glass

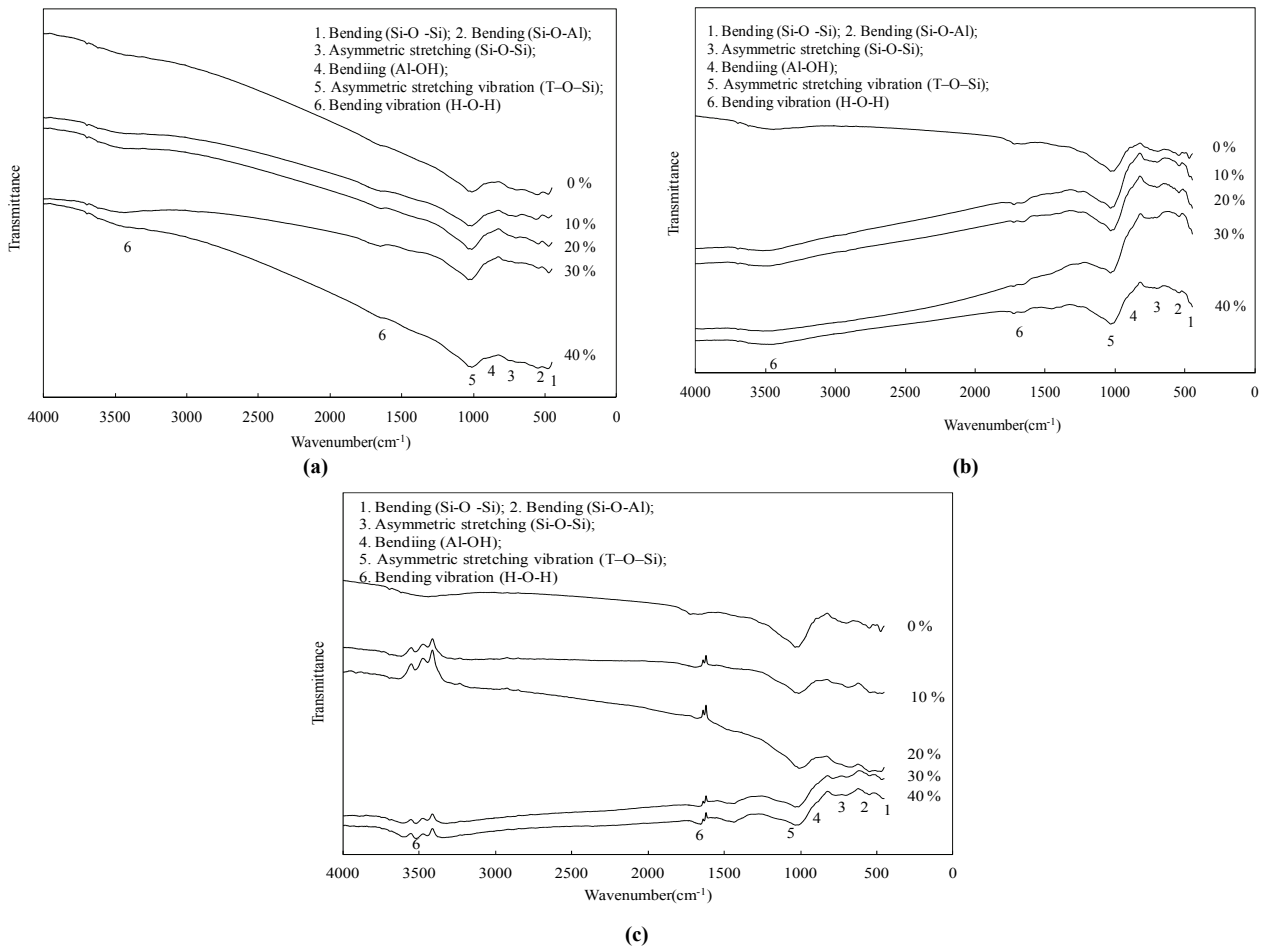


Fig. 7. FTIR patterns of geopolymers with and without solar panel waste glass. (a) 1 day, (b) 7 days, (c) 28 days

Table 2. FTIR absorption peaks for geopolymer at 28 days of curing

<i>Matrix</i>	<i>Wavenumber (cm⁻¹)</i>						
Waste glass	470	540	-		1008	1031	1087
Metakaolinite	474	540	811	-	-	1036	1068
Kaolinite	470	540	-	915	1008	1031	
0%	470	547	-	-	1012	1036	
10%	464	540	-	-	1010	1029	
20%	468	543	-	-	1006	-	
30%	-	543	-	-	1012	1033	
40%	-	545	-	-	1012	1031	

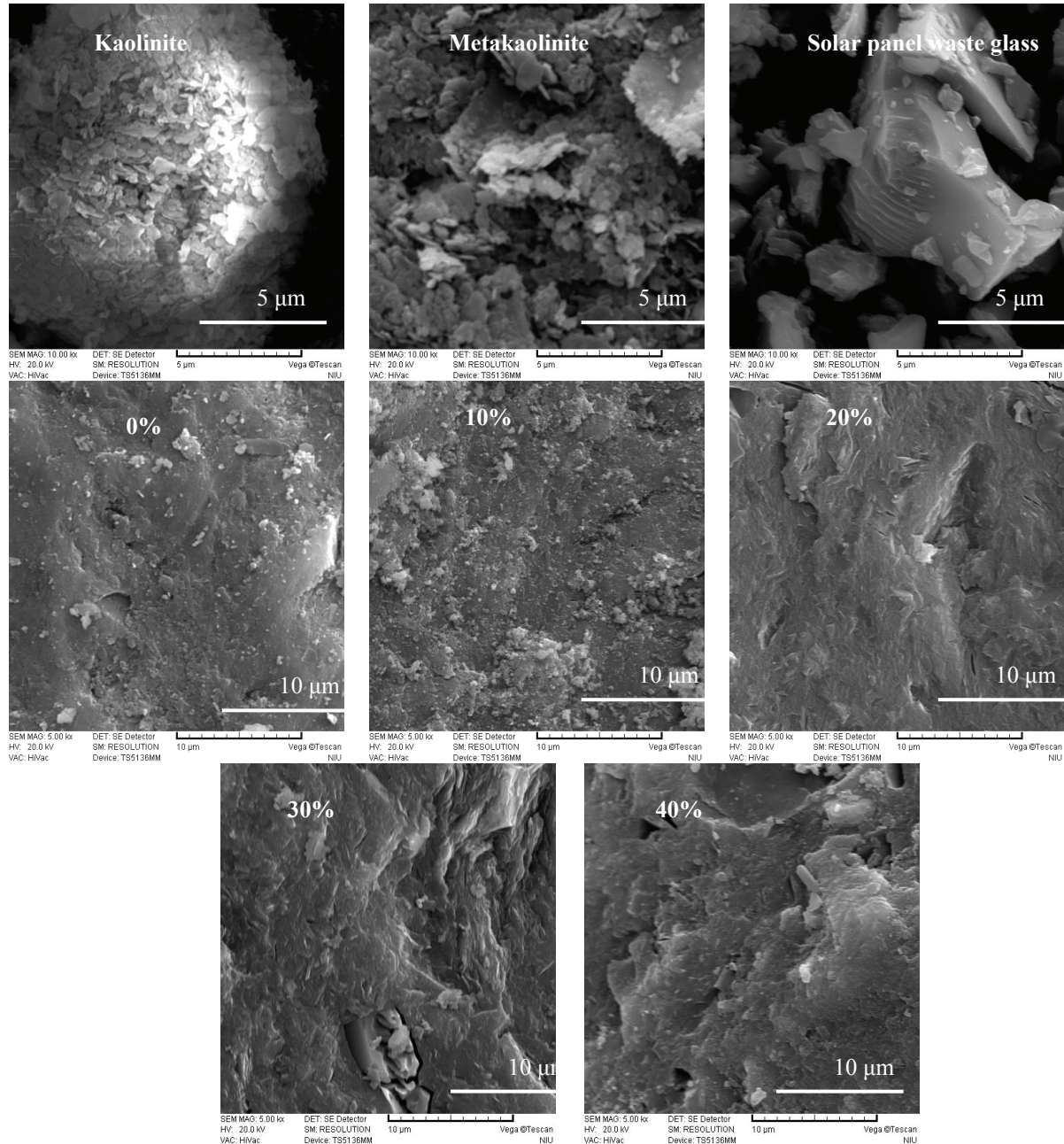


Fig. 8. SEM micrographs of raw materials and geopolymers with and without panel waste glass

3.6. SEM observation of geopolymers with and without solar panel waste glass

Fig. 8 shows the SEM micrographs of the raw materials and geopolymers with and without solar

panel waste glass that was aged for 28 days with S/L 0.8 and Ms 1.75. Kaolinite has a typical layered structure, such as metakaolinite. The micrograph of the raw materials indicated that the size of the particles in the solar panel glass exceeded those in

kaolinite and metakaolinite, the microstructures of which included an obvious interface and large pores. A previous study indicated that the main components of geopolymers are unreacted aluminosilicate particles and the gel phase (Kumar and Kumar, 2011; Lloyd et al., 2009). The observed gel with an amorphous structure is present in the geopolymer system and adheres to the product and unreacted particles. A geopolymer with more gel is denser, has a more homogenous microstructure and higher mechanical strength (Matthew and Brian, 2003).

The structure of the geopolymers with 10% waste glass was similar to that of the pure metakaolinite geopolymer, which was dense and homogenous. The SEM micrographs of the geopolymer with 30% and 40% waste glass differed considerably.

The main microstructure of geopolymer with 30% and 40% waste glass was inhomogeneous and non-compact, with unreacted material and several pores. These results suggest that the microstructures of stronger samples were more homogeneous and the microstructures of weak samples were highly inhomogeneous and incompact.

4. Conclusions

This study demonstrated the use of solar panel waste glass as a partial substitute for metakaolinite in the production of geopolymers. At 28 days of curing, the compressive strengths of geopolymers with 10% and 20% waste glass were 63 and 50 MPa, respectively. FTIR spectra indicated that the principal peaks were attributable to Si-O-Al bonds in the geopolymer. These results indicated that the optimal amount of waste glass in the geopolymer was 10%, which demonstrated the use of waste glass in the geopolymers by partial substitution of costly metakaolinite with the cheaper waste glass without considerable deterioration of geopolymer.

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CATHOLYTE-CONDITIONING ENHANCED ELECTROKINETIC REMEDATION OF Co- AND Pb- POLLUTED SOIL

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Abstract

The feasibility of catholyte-conditioning to enhance the electrokinetic (EK) remediation of cobalt and lead polluted soil has been investigated in this study. Electrokinetic experiments were conducted using an EK cell 10 cm in width, 10 cm in height, and 50 cm in length. Plate type electrode of graphite was used as electrode material. Two experiments were conducted under constant voltage condition (2 V/cm). The pH values of the soil significantly affect the removal of Co and Pb ions. Due to electrolysis reaction, soil pH increases near the cathode and without pH conditioning, metals precipitate as hydroxides. This problem is solved by the addition of nitric acid (0.1N) in the catholyte compartment. Significant movement of metals was observed through the soil with high removal efficiency. Results showed that catholyte conditioning using nitric acid increased the removal of cobalt and lead from the soil and, consequently, the maximum removal achieved was 73.84% and 62.88% for cobalt and lead, respectively. These EK tests indicate that the increased experimental time induced a higher removal efficiency of cobalt and lead. The results suggest that longer treatment periods will result in further transport of cobalt and lead in the sample. Also, it indicated that the highest quantities of cobalt and lead moved towards the catholyte, particularly at upper 5 cm. On the basis of the experimental results, we conclude that the electrokinetic remediation, using 0.1N HNO₃ as catholyte-conditioning, is suitable for extracting cobalt and lead from polluted soil.

Key words: Catholyte-conditioning, Cobalt, Enhanced electrokinetic, Lead, Nitric acid

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1. Introduction

Nowadays heavy metals pollution of soils has become a serious environmental problem in the world. Metals originate from a range of human activities including mining operations and landfills. Agricultural lands in the vicinity of these pollution sources have been seriously contaminated by metals (Reddy and Cameselle, 2009). Over the past few decades, several technologies have been applied to remove pollutants all over the world. A significant amount of electrokinetic remediation work for remediating heavy metals are available (Akram and Alshawabkeh, 2009; Probst and Hicks, 1993; Reddy, 2010; Saichek and Reddy, 2003). In recent decades, laboratory-scale and field scale studies have

shown that electrokinetic remediation can be effectively used to metal removal from soils (Bahemmat et al., 2010; Bulgariu et al., 2006; Ottosen et al., 2001; Reddy and Ala, 2005). A direct-current (DC) electric field is imposed on the contaminated soil. Contaminants migrated by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis. Electroosmosis is regarded as the phenomenon of water flow induced by application of an electrical field on porous media (Probst and Hicks, 1993), whereas, electromigration is characterized as the transport of ions under the influence of an electrical field (Acar and Alshawabkeh, 1993). Electrolysis of water is the dominant electron transfer reaction occurring at electrodes during the electrokinetic

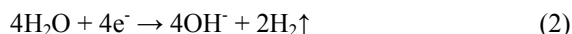
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process (Eqs. 1-2). As a result of electrolytic decomposition of electrolytes at the electrodes, H^+ and OH^- ions are generated at the anode and the cathode, respectively during the electrochemical remediation process as follows:

Oxidation at the anode:



Reduction at the cathode:



The generated H^+ and OH^- ions migrated through the soil by the DC electric field. Hydrogen ions produced in the process decrease the pH near the anode causing desorption of metallic contaminants from the soil solid phases. Then the dissolved metallic ions are removed from the soil solution by ionic migration and precipitation at the cathode (Acar and Alshawabkeh, 1993). On the other hand, increase in the hydroxide ion concentration causes an increase of the pH near the cathode.

One of the major problems encountered in the EK removal of heavy metals from soil is the precipitation of metal oxide/hydroxide near the cathode, where soil pH significantly increases due to production of hydroxide ion at the cathode (Baek et al., 2009). Where the pH changes significantly within a very short distance, creating a region called the pH front. Generally, this pH front is close to the cathode because the migration velocity of the hydrogen ions is higher than that of the hydroxide ions (Lee and Yang, 2000; Zhou et al., 2005). The pH front acts as a barrier for the removal of heavy metals, such as copper, lead, and zinc, from the soil during EK because the solubilities of most heavy metals are relatively low when the soil pH is high (Pavel and Gavrilescu, 2008; Zhou et al., 2003). The change in soil pH can change the chemical speciation of contaminants, rendering them immobile (Yeung and Gu, 2011). These precipitation reactions can be hindered by different enhancement techniques such as using purging solutions (HNO_3 , citric acid, HCl) or complexing agents (EDTA) and special electrodes and membranes (Virkutyte et al., 2002; Yeung et al., 1996).

Specific objectives of reservoir conditioning include: (1) precipitation of metal contaminants should be avoided and/or precipitates should be solubilized and mobilized; (2) electrical conductivity of the specimen should not be increased excessively in a short duration so as to avoid diminishing of the advective transport of contaminant by electroosmosis prematurely; (3) the electrolysis reaction at the cathode should possibly be depolarized to avoid the generation of OH^- ions and their transport into the specimen (Yeung and Gu, 2011). Accordingly, controlling soil pH is very important for the success of electrochemical remediation. The purpose of electrode reservoir conditioning is to maintain the pH of catholyte within appropriate ranges specific to the

contaminants being remediated. Cobalt is commonly obtained from Ni, Pb, Cu, and Fe ores as a by-product. The main industrial use of cobalt is in the production of high-grade steels, alloys, superalloys, and magnetic alloys. Acid conditions increase the availability of Cobalt as Co^{2+} . Cobalt was found to accumulate in hydrous oxides of Fe and Mn in soils (Bradl, 2005). As the soil pH is raised, Cobalt solubility decreases because of increased chemisorption on oxides and silicate clays, complexation by organic matter, and possibly precipitation of $Co(OH)_2$. Lead is the most abundant element among the heavy metals with an average content of approximately 15 ppm (Bradl, 2005). Under alkaline conditions, lead in the soil may become sediments of hydroxides [$Pb(OH)_2$] and carbonates ($PbCO_3$).

Soil pH determines the concentrations of hydroxide and carbonate in the soil solution, which play a crucial role in the formation of heavy metal complexes in soil (Virkutyte et al., 2002). To date, a very few studies have been reported the feasibility of electrokinetic remediation cobalt in real polluted soil. Unlike cobalt, numerous studies that use ideal soils such as kaolin spiked with a selected single contaminant (e.g. lead) to understand the contaminant transport processes have been reported. However, only a limited number of studies have been reported on real-world soils contaminated with a wide range of aged contaminants. Also, in literature, few studies have been encountered on the electro-remediation of heavy metals from natural polluted soil and compared its removal efficiencies in different depths.

In this study, we investigated the capability of electrokinetics with catholyte conditioning (0.1N HNO_3) for the simultaneous remediation of aged polluted soil with cobalt and lead at laboratory scale. Comparison of residual concentration of cobalt and lead after electrokinetic treatment was performed in two different depths and four different times.

2. Materials and methods

2.1. Soil sampling

Soil was taken from the site of a mine and several hundred kilograms were mixed. The soil had been polluted with cobalt and lead, and contained several other heavy metals at elevated concentrations due to the mining activity on the site. At the laboratory, the soil was sieved and the fraction smaller than 2 mm was used in electrokinetic experiments. Selected physicochemical properties of the soil were measured and are listed in Table 1.

The soil sample was submitted to a physicochemical characterization: pH, Electrical conductivity, moisture, texture and cation exchange capacity (CEC). The organic carbon (OC) content was determined by oxidation with 1 N potassium dichromate in acidic medium. Particle size distribution was determined by the hydrometer

method. Soil pH and EC were measured by employing a pH meter and EC meter. CaCO_3 content was determined by following equation (Eq. 3) (Sparks, 1996):

$$\text{CaCO}_3 (\%) = \frac{[(10 \times N_{\text{HCl}}) - (R \times N_{\text{NaOH}})] \times 0.05 \times 100}{W_t} \quad (3)$$

where N_{HCl} is the normality of the HCl solution, R is the volume of NaOH solution used (ml), N_{NaOH} is the normality of the NaOH solution, and W_t is the weight of air-dried soil (g).

Table 1. Selected physicochemical properties of soil

Soil property	
Sand (%)	56
Silt (%)	22
Clay (%)	22
pH	8.2
Electrical Conductivity (ds m^{-1})	1.493
Organic Carbon (%)	0.86
Soil Saturation Percent (%)	38.88
CEC ($\text{cmol}_+ \text{kg}^{-1}$)	21.9
Carbonate Content (%)	12.07
Pb (mg kg^{-1} soil)	2500
Co (mg kg^{-1} soil)	19.83

2.2. Electrokinetic set up

The experimental apparatus is shown schematically in Fig. 1. Electrokinetic experiments were conducted in a $50 \times 10 \times 10 \text{ cm}^3$ plexiglass cell. The two electrode compartments (with 1000 mL working volume) were placed at each end of the sample compartment. On both sides, two graphite plate electrodes ($10 \text{ cm} \times 5 \text{ cm} \times 1 \text{ cm}$) were used to apply the electric field. Two sheets of filter paper (Whatman 42) were used to isolated soil particles and the electrolyte solution reservoirs. The total length of the soil column was 30 cm.

The solutions in the electrode compartments were stirred continuously. Each electrode compartment was changed (refreshed) daily.

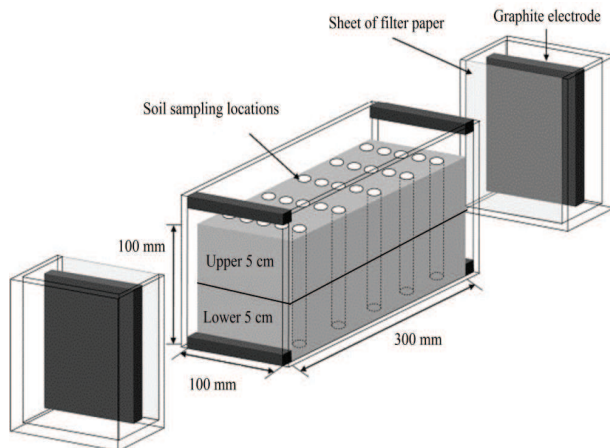


Fig. 1. Schematic of the electrokinetic cell apparatus

2.3. Experimental conditions

Initially, for each electrokinetic test, approximately 5 kg of dry soil were saturated with 2 L of water (according to saturation percent) and mixed in a polyethylene container with a stainless spatula. After saturation, the electrokinetic cell was compactly filled with the saturated soil. Experimental conditions are summarized in Table 2. Exp. 1 is a conventional electrokinetic experiment, and in Exp. 2 used 0.1N HNO_3 as a catholyte-conditioning fluid to control the catholyte pH (6-7) which enhance desorption of Co and Pb from soil. A constant voltage gradient of 2 V/cm was applied to the electrode, and the electrokinetic process was carried out for 20 d.

Table 2. Experimental condition of electrokinetic process

Exp. no.	Anolyte purging solution	Catholyte purging solution	Duration (days)	Electric potential (V/cm)
1	Distilled water	Distilled water	5, 10, 15, 20	2
2	Distilled water	0.1N HNO_3	5, 10, 15, 20	2

2.4. Analytical procedure

During the electrokinetic treatment, the electric current was measured hourly, and the soil pH was measured daily at five different locations: 5, 10, 15, 20 and 25 cm from the anode. Moreover, after 5, 10, 15 d of experimental time, soil samples were taken from same positions by a glass tube. Also, the soil samples taken from both upper 5 cm and lower 5 cm at these location after 20 d. The samples were oven dried and then digested by HNO_3 (4N) (Richards et al., 1998). The solution samples from the acid digestion procedures were analyzed using an AAS (Shimadzu, Japan). Also, removal efficiency of metal ions by electrokinetic is defined as following equation (Eq. 4):

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (4)$$

where, C_0 is initial metals concentration (mg kg^{-1}) of soil, and C_f is the final concentration of metals (mg kg^{-1}) after electrokinetic treatment in soil.

3. Results and discussion

3.1. Distribution of soil pH after electrokinetic treatment

As described above, the anode region becomes acidic due to H^+ generation and the cathode region becomes alkaline due to OH^- generation during EK processes. The variation in the pH of the soil specimen was measured directly using a pH probe during electrokinetic remediation and is shown in Fig. 2.

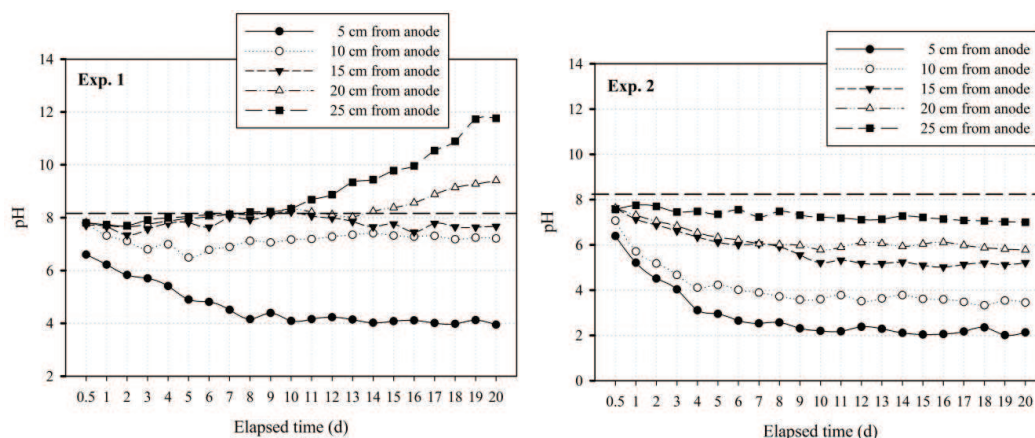


Fig. 2. The variation of pH of soil during electrokinetic experiment

In Exp. 1, where conditioning was not performed, the pH changed to below 4 from the initial 8.2 near the anode and above 12 near the cathode (25 cm from anode).

These results are in accordance with the findings reported in various studies (Bahemmat et al., 2010; Kim et al., 2009). In typical electrokinetic remediation without electrolyte conditioning (Exp. 1), the H^+ ions were transported towards the cathode by electromigration and electroosmosis, while OH^- was moved towards the anode. However, H^+ travels at a velocity 1.8 times faster than OH^- (Acar and Alshawabkeh, 1993). Whereas H^+ enhanced desorption of heavy metals, OH^- significantly declined the mobility of the metal ions because of $Me(OH)_2$ precipitation (Lee and Yang, 2000). It is pivotal, to maintain an acidic pH in the soil and to prevent hydroxide precipitation (Yeung and Gu, 2011). The transport of the base front from the cathode compartment to the soil has several unfavorable effects that result in a decrease in the effectiveness of the electrokinetic remediation (Virkutyte et al., 2002).

Acidic electrolytes such as HNO_3 , has been used for this purpose. Electrolyte pH conditioning is a feasible and convenient way to adjust soil pH during EK process. In Exp. 1 without catholyte pH conditioning, the pH in the section of soil close to the cathode quickly increased to above initial pH at 10 d. For Exp. 2 with catholyte pH conditioning, the pH in the section of soil close to the anode was even decreased to about 2 in the later stage. In the experiment without catholyte conditioning, soil pH increased from 2 close to the anode to more than 11 close to the cathode. This is a typical soil pH variation for EK remediation (Acar and Alshawabkeh, 1993; Reddy, 2010; Saichek and Reddy, 2003).

The pH in the central section of the soil ranged between the values found at the anode and the cathode. The pH increased as the soil became far away from the anode, and the pH in the middle of the soil cell maintained about at the initial value of 8.2. The much lower soil pH near anode in Exp. 2 than in Exp. 1 was ascribed to the production of more H^+ at

anode in Exp. 2 with higher current (Fig. 3), which exceeded the buffering capacity of anolyte. The pH distribution in Exp. 2, where conditioning was performed, was rather even. In relation to pH, as it was expected, the catholyte presented predominantly an alkaline pH and the anolytes an acid pH which varied between 3 and 4, if they are not controlled (Lee and Yang, 2000).

3.2. Variation of current density

Fig. 3 shows the comparison of current variation with elapsed time for Exp. 1 and Exp. 2. The development of the current density is demonstrated for 24 h that it is average of 20 d. The ions move in consequence of the process of electromigration and electro-osmosis, and as the concentration of ions reduce in the soil with treatment time, decreasing the current intensity (Reddy and Ala, 2005).

In Exp. 2, the electrical current was higher than in Exp. 1 in the same time. Kim et al. (2009) reported that under a constant current the introduction of hydrogen ions into the soil by acidic circulation using HNO_3 can decrease the voltage gradient and resistance of the soil and enhance the dissolution of soil minerals. At the very beginning, current density increased rapidly and peaked at 26 mA cm^{-2} . Then, the current decreased, dropping to a value below 2 mA cm^{-2} within the first 20 h. Finally, the electric current stabilized at a low value that ranges from 1 to 2 mA cm^{-2} with increased treatment time. The maximum and minimum current recorded in the 6 h and 24 h were, respectively, about 26 and 1.4 mA cm^{-2} .

The changes in current density were almost similar in all days because each electrode compartments changed (refreshed) daily and solute ions in those depleted. The increase of current intensity is attributed to significant H^+ and OH^- ions generated at the anode and cathode, respectively, due to electrolysis of water (Acar and Alshawabkeh, 1993). The increase of ion concentration in the electrode compartments results in the decreasing of the electric resistance and therefore, increasing of the

electric current (Reddy and Ala, 2005; Reddy and Karri, 2006).

Furthermore, the increased mobility of ions in the soil as a result of dissolution of precipitated salts and desorption of adsorbed ions (Reddy et al., 2011) also contributes to the electric current. Also, the OH⁻ ions electrogenerated at the cathode will increase the soil pH close to the cathode end. High pH decreases the solubility of metal ions, forming precipitates that diminish the total amount of ions available to transport (Virkutyte et al., 2002).

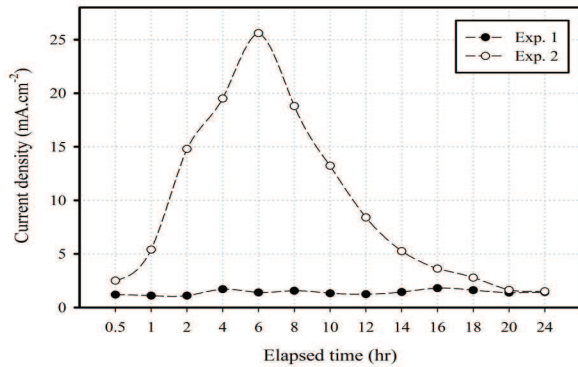


Fig. 3. Example of typical evolution of daily current density during electrokinetic treatment

It results in a decreasing electric current intensity. The increase in extraction of the heavy metals and other ions caused a decrease in the electrical resistance of the soil. Thus, the current density increased gradually over a period of 6 h, decreased suddenly, and remained low thereafter. In general, the current values initially increased to a maximum value within a short time and then reduced and stabilized.

For Exp. 2 test, current increased rapidly within the first 6 h of the testing and then started to decrease and stabilize thereafter. As the ions migrated towards the electrolyte compartments, however, the current gradually declined. After approximately 20 h of voltage gradient application, the current for Exp. 1 and Exp. 2 tests stabilized at almost the same level (i.e., 1 mA). High current was measured due to the partial solubilization of salt precipitates resulting in higher ionic concentration in pore-water (Virkutyte et al., 2002; Saichek and Reddy, 2003).

However, with increased elapsed time, these ions are depleted as they migrate into the electrolyte compartments (Reddy and Karri, 2006). At the same time, ions constantly generated near the anode had high mobility and were transported through the soil due to different transport processes including electromigration and electroosmosis (Acar and Alshawabkeh, 1993).

3.3. Cobalt and lead distribution after electrokinetic treatment

Extraction of the remaining cobalt and lead in the soil samples was performed according to the Section 2.3. General remediation results are given in Tables 3 and 4. Table 3 includes normalized concentrations of Co and Pb (C/C_0) in the soil, after the unenhanced electrokinetic treatment (Exp. 1), and Table 4 shows the details of the normalized concentrations of Co and Pb (C/C_0) in the soil, after the catholyte-conditioning enhanced electrokinetic (Exp. 2), under the different time. As shown in Tables 3 and 4, results indicated that the electrokinetic remediation efficiency of cobalt can be largely enhanced by catholyte conditioning. At the case of unenhanced electrokinetic (Exp. 1), only 15.46% of cobalt was removed.

The cobalt concentrations in the soil (Table 4) decreased compared to the initial concentration and the lowest concentrations were found in Exp. 2 near the anode. In some sections metal concentrations increased compared to the initial concentrations ($C/C_0 > 1$), because of the accumulation of metals.

The migration and transport of the cobalt was higher under condition of catholyte conditioning using an acidic solution because cations including metal ions can be easily desorbed into the pore solution from a soil surface in an acidic condition (Ouhadi et al., 2010; Xiu and Zhang, 2009). Hence, these desorbed metal ions can easily be transported by electromigration under an electric field (Probstein and Hicks, 1993; Virkutyte et al., 2002).

The lead removal efficiencies were 21.23% and 38.14% for Exp. 1 and Exp. 2, respectively. Similar to the results for cobalt removal, catholyte conditioning with an acidic solution helped to enhance lead removal efficiency.

Table 3. Normalized concentrations of heavy metals (C/C_0)^{*} in the soil, after the electrokinetic treatment^{**} (Exp. 1), under the different time

Normalized concentrations of heavy metals (C/C ₀)											
	Cobalt						Lead				
	Distance from anode (cm)						Distance from anode (cm)				
Time (d)	5	10	15	20	25		5	10	15	20	25
5	0.885	1.111	0.864	1.099	0.785		0.849	0.895	0.967	1.091	0.950
10	1.011	0.996	1.022	0.859	0.750		0.759	0.890	0.964	1.132	0.873
15	0.868	0.922	0.892	0.812	0.873		0.683	0.868	0.879	0.958	0.837
20	0.811	0.757	0.934	0.912	0.811		0.674	0.778	0.860	0.890	0.734

^{*} C_0 : Initial concentration; C : Final concentration

^{**}Mean values of the five replicates.

Table 4. Normalized concentrations of heavy metals (C/C_0)* in the soil, after the electrokinetic treatment** (Exp. 2), under the different time

Normalized concentrations of heavy metals (C/C ₀)											
	Cobalt						Lead				
	Distance from anode (cm)						Distance from anode (cm)				
Time (d)	5	10	15	20	25		5	10	15	20	25
5	1.093	1.071	0.809	0.774	0.904		0.761	0.969	0.919	1.076	0.804
10	0.776	1.220	1.061	1.021	0.773		0.603	1.234	0.852	0.739	0.758
15	0.461	0.818	0.818	0.901	0.604		0.474	0.939	0.910	0.790	0.760
20	0.262	0.883	0.366	0.964	0.395		0.371	0.674	0.678	0.696	0.672

* C_0 : Initial concentration; C: Final concentration

**Mean values of the five replicates.

For all experiments, lead accumulated in the cathode section because Pb^{2+} ions from the anode compartment met OH^- from the cathode compartment and precipitated as $Pb(OH)_2$, and were partially removed from the anode section because lead in the electrokinetic process became cationic and moved towards the cathode, most probably as free Pb^{2+} ions in the pore fluid (Lee and Yang, 2000). In catholyte conditioning using an acidic purging solution, the overall cobalt and lead removal efficiencies were 42.58% and 38.14%, respectively.

In Exp. 1 where catholyte conditioning was not performed, the cobalt removal efficiency was lower than that for catholyte conditioning: 15.4%, and 38.1%, respectively. According to Chung and Kang (1999), the transport of lead (II) at low levels of concentration is slower because almost all of the lead is adsorbed to the soil particle. Using 0.1 N nitric acid as a purging solution, it seems that after initial 10 d of treatment cobalt and lead accumulated in the middle of the cell. As a result of the low pH close to the anode, lead and cobalt existed as Pb^{2+} and Co^{2+} , and migrated towards the cathode (Hamed et al., 1991; Virkutyte et al., 2002). By the end of the experiment, 62.88% of lead had been removed from the soil close the anode. According to Puppala et al. (1997), soil pH should be kept below 6 to hinder these precipitation reactions. Virkutyte et al. (2002) report that these reactions occur at their lowest level when pH is between 4 and 4.5.

Cobalt seems to follow the almost same route as lead. An amount of cobalt dissolved close to the anode accumulated in the middle of the cell. Presence of peak concentrations of cobalt in the middle of column, suggests that while Co is transported from anode to cathode by electromigration. By the end of the experiment, about 73.83% of cobalt had been removed from the soil close the anode. As expected, the increase in remediation time from 5 to 20 days increases the removal efficiency of cobalt 7% to 42.58%, respectively (Exp. 2).

From the analysis of the results for different remediation time, it can be concluded that 9.38% to 38.14% of the total lead removed from soil at 5 to 20 days, respectively. Higher remediation times would increase the cobalt and lead removal at the soil section close to the anode. The results suggest that longer treatment periods will results in further transport of cobalt and lead in the soil.

3.4. Comparison of residual concentration of cobalt and lead after electrokinetic treatment in two different depths

Fig. 4 illustrates the results of the remaining concentration cobalt after the experiment was completed in two different depths. As it can be seen, more than 70% of the initial Co and more than 60% of the initial Pb were removed from the soil with the application of electric field in areas close to the anode (0-5cm). After 20 days of Exp. 1, the residual concentration of cobalt in the soil sections after the electrokinetic treatment decreased and removal efficiency of cobalt was in two depths almost similar. In the lower 5 cm, cobalt removal is less than in the upper 5 cm as shown in Fig. 4.

Compared with the control, lead concentration extracted by HNO_3 clearly decreased in the sections near the anode, which is in good agreement with the fact that Pb^{2+} migrates from anode toward cathode. As seen from Figs. 4 and 5, the difference of between removal efficiency of lower and upper 5 cm was not significant for Exp. 1, while for Exp. 2 in upper 5 cm, the removal efficiency was higher than in lower 5 cm in the same locations particularly for cobalt. The general trend of decrease in the removal efficiency as distance from the anode increases is also seen in these electrokinetic experiments. The removal efficiency drops below 25% for all soil sections, and for both cobalt and lead in lower 5 cm in the Exp. 1.

The highest removal efficiency comes from the section closest to anode, as expected. When the soil at the section closest to anode were analyzed, the results are comparable with the findings in various studies in which the same conditioning solution was treated (Kim et al., 2009, 2011; Ryu et al., 2011). In the Exp. 2, when the soil at the lower 5 cm were analyzed, it can be seen that the removal efficiency for cobalt and lead is lower than 30% except for Pb in area close to the anode (0-5cm), which is 60% (Fig. 5).

4. Conclusions

The present study has demonstrated the possibility to remove the cobalt and lead in soil when submitted to an electric field concurrently, as well as the applicability of the electrokinetic (EK) process to remove them from two different depths.

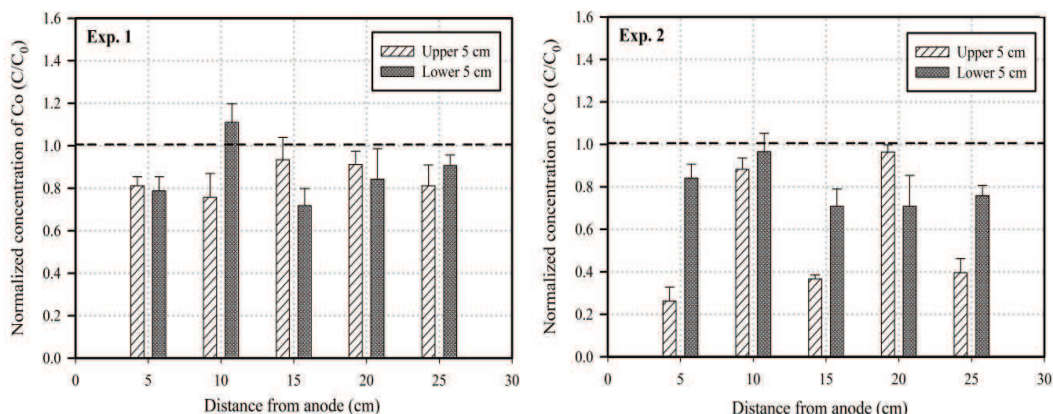


Fig. 4. Comparison of residual concentration of Co after electrokinetic remediation in upper and lower 5 cm, Error bars represent $\pm$ one standard error ($n = 3$)

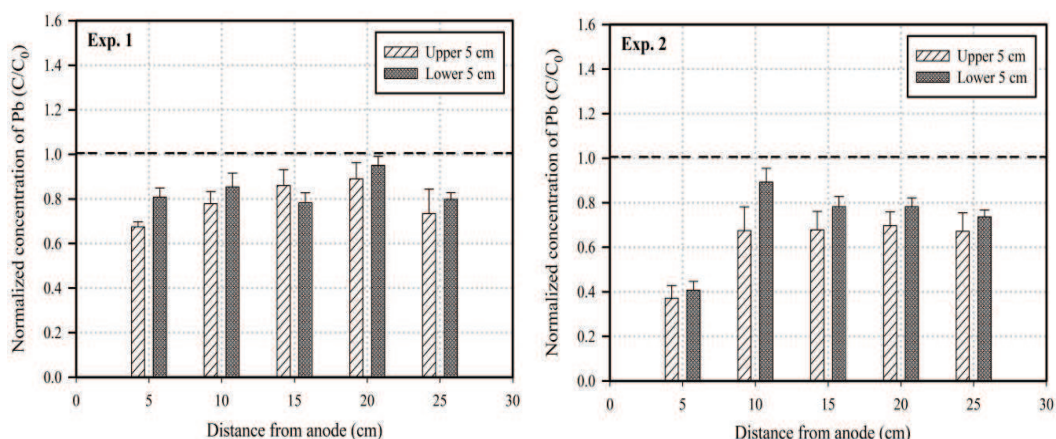


Fig. 5. Comparison of residual concentration of Pb after electrokinetic remediation in upper and lower 5 cm, Error bars represent $\pm$ one standard error ($n = 3$)

The results indicated that with application of electric field in soil, acidic conditions dominated in the soil cell, and the highest quantities of cobalt and lead moved towards the catholyte, particularly at upper 5 cm. Also, this shows that catholyte conditioning (0.1N nitric acid) is a very effective enhancement method to remove cobalt and lead from polluted soil in electrokinetic remediation.

Acknowledgements

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PERFORMANCE ANALYSIS FOR AN IRREVERSIBLE COMBINED THERMIONIC-THERMOELECTRIC GENERATOR WITH FINITE RATE HEAT TRANSFER

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Abstract

A model of an irreversible combined thermionic-thermoelectric generator with internal and external irreversibilities is established in this paper. The performances of the combined generator, in which the heat transfers obey radiative heat transfer law, are analyzed and optimized by using the combination of finite time thermodynamics and non-equilibrium thermodynamics. The general expressions for power output and efficiency versus drop voltage are derived. The influence of finite rate heat transfer on the performance of the combined device is extensively explored through numerical calculations. Moreover, the effects of some design parameters, i.e., the working electrical current of the thermoelectric circuit, the number of thermoelectric generating elements, and the heat sink temperature are analyzed by using detailed numerical examples. The performance of the combined generator with or without considering finite rate heat transfer is compared with that of an independent vacuum thermionic generator considering external finite rate heat transfer. The results obtained herein may provide some guidelines for the design and application of practical combined thermionic-thermoelectric generators.

Key words: combined thermionic-thermoelectric generator, finite rate heat transfer, finite time thermodynamics, performance analysis

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1. Introduction

The performance of thermionic power generation systems has been extensively explored since the 1950s (Baksht et al., 1978; Gabor, 1961; Hatsopoulos and Gyftopoulos, 1973; Hatsopoulos and Kaye, 1958; Houston, 1959; Koeck and Nemanich, 2010; Lee et al., 2009; Rasor, 1960; Smith et al., 2009a; Wilson, 1959). In thermionic power generation devices, a hot cathode contacting with a heat source can emit electrons which are then absorbed by a cold anode whose Fermi level is more negative than that of the cathode; and electric current can be produced in the external circuit connecting the cathode and anode (Baksht et al., 1978; Hatsopoulos

and Gyftopoulos, 1973). Compared with conventional power generation device, thermionic generator has the advantage of converting thermal energy directly into electric energy without using mechanical moving parts and environmentally harmful working fluids. However, due to the lack of stable electrode materials with sufficiently low work function, practical thermionic power generator usually requires a high temperature (usually higher than 1000K) heat source to generate a practically useful current. At high temperatures, vacuum thermionic power generators are capable of achieving high efficiencies (Cayless, 1961; Ingold, 1961; Lawless and Lam, 1986; Robinson and Shimada, 1976). Besides power generation, thermionic

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emission can also be used for refrigeration. The theory of thermionic refrigeration was first presented by Mahan (1994) as a vacuum diode. Many research works have been carried out on vacuum (Gerstenmaier and Wachutka, 2007; Hishinuma et al., 2001, 2002, 2003; O'Dwyer et al., 2009; Shakouri and Bowers, 1997; Smith et al., 2009b) and solid-state (Bian and Shakouri, 2006; Lough et al., 2001; Mahan and Woods, 1998; O'Dwyer et al., 2007; Shakouri et al., 1999; Ulrich et al., 2002; Vining and Mahan, 1999) thermionic refrigeration devices.

Similar to thermionic devices, thermoelectric devices can also serve both as a generator and a refrigerator (Angrist, 1992; Bell, 2008; DiSalvo, 1999; Ma and Riffat, 2003; Rowe, 1995). Essentially, the energy conversions in both thermionic and thermoelectric devices are induced by the transport of electrons. In thermionic devices, the transport of electron is ballistic; while in thermoelectric devices, the transport of electron is diffusive. Considering the similarities between the two kinds of devices, some researchers compared the performances of thermoelectric with those of the thermionic refrigeration systems (Nolas and Goldsmid, 1999; Ulrich et al., 2001).

However, contrary to the high working temperature of thermionic devices, thermoelectric devices can achieve energy conversion at rather low temperatures. Some authors (Xuan, 2002; Xuan and Li, 2003) therefore proposed the models of combined thermionic-thermoelectric energy conversion systems in which thermoelectric modules were used to improve the performance of thermionic devices. Xuan (2002) presented a novel combined thermionic-thermoelectric refrigerator by replacing the passive metal conductor with an active P-type thermoelectric element and shown that due to the Peltier cooling power of the thermoelectric element, the combined thermionic-thermoelectric refrigerator was more effective and efficient than thermionic or thermoelectric device alone. Xuan and Li (2003) later proposed a combined thermionic-thermoelectric generator model in which a thermoelectric generator was utilized to make use of the rejected heat from the collector of the thermionic generator and produces additional electrical power. The optimum performance of the combined generator has been analyzed and it is shown that the combined generator system has both improved efficiency and power output.

However, in Xuan and Li's work (Xuan and Li, 2003), the performance analysis and optimization for the combined generator were mainly based on non-equilibrium thermodynamics and the generator was assumed to be thermally insulated from surroundings in which the internal and external finite rate heat transfer processes were ignored. In order to obtain more practical and accurate results for the combined thermionic-thermoelectric generator, the internal and external finite rate heat transfer of the device cannot be neglected in the analysis. The theory of finite time thermodynamics (FTT) (Andresen, 1983, 2011;

Bejan, 1996; Berry et al., 1999; Chen and Sun, 2004; Chen et al., 1999; Hoffmann et al., 1997; Sieniutycz and Jezowski, 2009; Sieniutycz and Shiner, 1994; Stanciu et al., 2011; Tirca-Dragomirescu et al., 2011) is a powerful tool for performance analysis and optimization of practical thermodynamic processes and devices. The irreversibility of finite rate heat transfer is one of the most important facts concerning the FTT theory. So far, the FTT performance for the combined thermionic-thermoelectric generator has not been investigated in the open literature. Therefore, the present work aims to analyze in detail the influence of finite rate heat transfer processes on the performance of the combined thermionic-thermoelectric generator.

On the basis of the exoreversible model of combined generator presented by Xuan and Li (2003), an irreversible combined thermionic-thermoelectric generator model considering internal and external irreversibilities of finite rate transfers is established. The general formula for power output and efficiency of the combined generator are derived by assuming that the heat transfer in the system obeys radiative heat transfer law. The optimum power and efficiency performances of the combined device are obtained and the effects of some major design parameters, i.e., the working electrical current of the thermoelectric circuit, the number of thermoelectric generating elements, and the heat sink temperature are analyzed through numerical examples.

The effect of finite rate heat transfer is investigated by comparing the performances of the combined generator considering finite rate heat transfer with those obtained by traditional analysis without considering finite rate heat transfer. The performance of the combined generator with or without considering finite rate heat transfer is further compared with that of the independent vacuum thermionic generator considering external finite rate heat transfers.

2. Model of an irreversible combined thermionic-thermoelectric generator

Fig. 1 shows a schematic diagram of an irreversible combined thermionic-thermoelectric generator with internal and external finite rate heat transfers. The whole system mainly consists of two parts: the thermionic power generation part and the thermoelectric power generation part. The two parts are thermally connected in series but electrically isolated with the two parts have their own resistive loads R_1 and R_2 . For an independent thermionic generator, the heat leaving the collector is dissipated into the cold heat reservoir and wasted. While for the present combined generator, the thermoelectric generator is thermally connected to the collector of the thermionic generator and will produce additional electric power, thus the heat leaving the collector can be further utilized and the performance of the entire device can be improved. The combined thermionic-thermoelectric converter is a solid-state energy

conversion device without moving parts and gaseous or liquid working fluids. Therefore, practical combined thermionic-thermoelectric generators such as solar-powered combined thermionic-thermoelectric converters are particularly suitable for space applications. For example, they can be used in the spacecrafts due to its ability to withstand intense irradiation and heat fluxes.

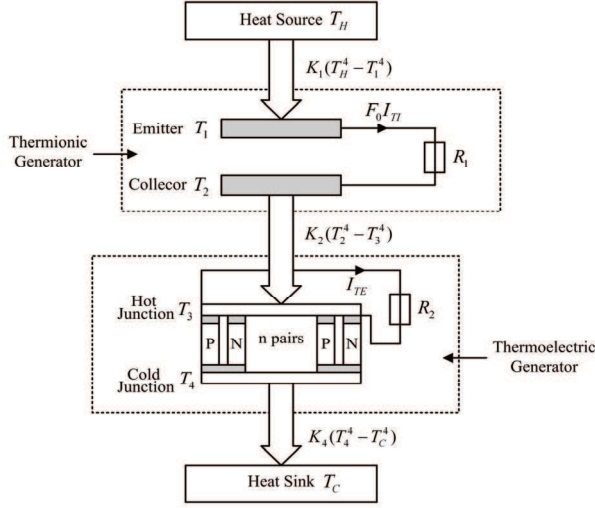


Fig. 1. Schematic diagram of an irreversible combined thermionic-thermoelectric generator with finite rate heat transfer

Actually, the external heat transfer between the device and external heat reservoir as well as the internal heat transfer between the thermoelectric part and the thermionic part inside the combined device are all inherently irreversible and have great influences on the performance of the combined power generation device. The irreversibility of finite rate heat transfer, which is not considered in the analysis when using non-equilibrium thermodynamics, is one of the most important considerations in FTT theory.

In the past few decades, the theory of FTT was widely applied to the performance analysis and optimization for various conventional thermodynamic processes and devices and thermoelectric energy conversion systems. The performances of single-stage thermoelectric generators (Chen, 1996; Chen et al., 2002, 2007; Gordon, 1991) and refrigerators (Goktun, 1995; Luo et al., 2003; Xuan et al., 2002) with single-element and multi-element, two-stage thermoelectric generator (Chen et al., 2005b) and refrigerator (Chen et al., 2005a; Yu et al., 2007) with internal and external irreversibilities have been optimized by using FTT theory. In addition, the FTT performances of independent thermionic power generators (Bhattacharyya, 1999; Erbay and Yavuz, 1997; Wang et al., 2013; Wu, 1992) and refrigerators (Chen et al., 2010; Ding et al., 2012; Pan and Lin, 2008) have also been investigated by some researchers.

In the following two sections, the heat flows

in the thermionic and thermoelectric parts will be derived, respectively.

2.1. Heat flow in thermionic part

As to the thermionic part of the combined system, the thermionic generator works while there is a net flow of electrons from the emitter to the collector. In the thermionic generator, there exists a potential drop V across the external load R_1 . Externally, the emitter at temperature T_1 exchanges heat with the heat source at temperature T_H , and the collector at temperature T_2 exchanges heat with the hot junction of the thermoelectric generator at temperature T_3 . Finite rate heat transfer processes cause the external irreversibility. Here, the hot junction of the thermoelectric generator is served as the heat sink of the thermionic generator and the relation $T_H > T_1 > T_2 > T_3$ holds.

It is assumed that the combined thermionic-thermoelectric generator is designed to construct a solar-driven power generation device for space application. In this circumstance, the working temperature is high and it is more reasonable to use the radiative heat transfer law to describe the heat transfer processes between the device and the external heat reservoirs (Incropera and DeWitt, 1985; Janna, 2000). Thus, assuming that the heat transfer inside the device obeys radiative heat transfer law, the heat flow rate ($Q_{H,TE}$) flowing from the heat source into the emitter and heat flow rate ($Q_{C,TE}$) flowing from the collector to the hot thermoelectric junction are defined by Eqs. (1 and 2):

$$Q_{H,TE} = K_1(T_H^4 - T_1^4) \quad (1)$$

$$Q_{C,TE} = K_2(T_2^4 - T_3^4) \quad (2)$$

In above two equations, K_1 is the heat conductance between the heat source and emitter; K_2 is the heat conductance between collector and hot thermoelectric junction.

The following assumptions are made for the thermionic generator: (a) the electrode space is evacuated, thus only the heat transfer of thermal radiation exists between the electrodes; (b) the distance between the electrodes is kept small enough for the space charge effects to be negligible. Vacuum thermionic devices with the electrode gap in the order of micrometers are available with modern fabricating technology (Hatsopoulos and Gyftopoulos, 1973). And vacuum thermionic devices with even small electrode gaps, such as nanometer vacuum thermionic power generation and refrigeration devices have also been reported (Chua et al., 2004; Gerstenmaier and Wachutka, 2007; Hishinuma et al., 2001; 2002, 2003; Lee et al., 2009).

According to the Richardson's equation, the thermionic electrical current (I_1) leaving the emitter per unit area and the electrical current (I_2) leaving the collector per unit area can be given by (Hatsopoulos and Gyftopoulos, 1973; Wilson, 1959) (Eq. 3):

$$I_1 = A_0 T_1^2 \exp\left(-\frac{q\phi_2 + qV}{k_B T_1}\right), I_2 = A_0 T_2^2 \exp\left(-\frac{q\phi_2}{k_B T_2}\right) \quad (3)$$

In Eq. (3), $A_0 \approx 1.2 \times 10^6 \text{ Am}^{-2} \text{ K}^{-2}$ is Richardson's constant, q is the charge of an electron and k_B is the Boltzmann's constant, ϕ_2 is the work function of the collector. In this case, it is assumed that the conventional current from the emitter to be in the positive direction. Thus, the electric current density (I_{II}) in the interelectrode space is given by Eq. (4):

$$I_{II} = I_1 - I_2 \\ = A_0 \left[T_1^2 \exp\left(-\frac{q\phi_2 + qV}{k_B T_1}\right) - T_2^2 \exp\left(-\frac{q\phi_2}{k_B T_2}\right) \right] \quad (4)$$

According to the law of energy conservation, the supplied heat from the heat source to the emitter must be equal to the total heat leaving the emitter. The total heat transferred from the emitter includes the heat caused by the electrons flowing into and out of the emitter, the radiation heat, and the conducted heat through the electrical leads and the structural components that can be connected to the emitter. The heat conducted by the electrical leads and the structural components are relatively small compared to the other two kinds of heat flows. Therefore, the heat conduction processes through the electrical leads and the structural components are ignored in the present analysis, and there exist only two kinds of heat flows inside the thermionic generator: one is the heat transport between the electrodes due to the emission of electrons; and another is the radiation heat flow between the emitter and collector. As a result, in thermionic part, the voltage V across the external load is equal to the electrode output voltage.

The first kind of heat flow, i.e., the heat flow rate leaving the emitter ($\dot{Q}_1$) and that entering the collector ($\dot{Q}_2$) per unit area due to the emitted electrons are given by (Wilson, 1959; Hatsopoulos and Gyftopoulos, 1973) (Eqs. 5 and 6):

$$\dot{Q}_1 = (\phi_2 + V + 2k_B T_1/q) I_1 - (\phi_2 + V + 2k_B T_2/q) I_2 \quad (5)$$

$$\dot{Q}_2 = (\phi_2 + 2k_B T_1/q) I_1 - (\phi_2 + 2k_B T_2/q) I_2 \quad (6)$$

It is assumed that the electrodes are perfect thermal radiators. Thus, the second kind of heat flow, i.e., the thermal radiation per unit area from the emitter to the collector is given by Eq. (7):

$$\dot{Q}_R = \mu \sigma (T_1^4 - T_2^4) \quad (7)$$

In the equation, μ is the thermal emissivity of the electrode surfaces, and σ is the Stefan-Boltzmann constant.

By using the theory of non-equilibrium thermodynamics and combining Eq. (3) with Eqs. (5)–(7), one can obtain the rate of total heat ($\dot{Q}_H$) leaving the emitter per unit area and the rate of total heat ($\dot{Q}_C$) entering the collector per unit area (Eqs. 8 and 9):

$$\dot{Q}_H = \dot{Q}_1 + \dot{Q}_R \\ = (\phi_2 + V + 2k_B T_1/q) A_0 T_1^2 \exp\left(-\frac{q\phi_2 + qV}{k_B T_1}\right) - \\ (\phi_2 + V + 2k_B T_2/q) A_0 T_2^2 \exp\left(-\frac{q\phi_2}{k_B T_2}\right) + \\ \mu \sigma (T_1^4 - T_2^4) \quad (8)$$

$$\dot{Q}_C = \dot{Q}_2 + \dot{Q}_R \\ = (\phi_2 + 2k_B T_1/q) A_0 T_1^2 \exp\left(-\frac{q\phi_2 + qV}{k_B T_1}\right) - \\ (\phi_2 + 2k_B T_2/q) A_0 T_2^2 \exp\left(-\frac{q\phi_2}{k_B T_2}\right) + \mu \sigma (T_1^4 - T_2^4) \quad (9)$$

The heat flow in the thermionic part is in balance. Thus, combining Eqs. (1), (2), (8) with (9) gives the following heat balance equations (Eqs. 10 and 11).

$$Q_{H,II} = K_1 (T_H^4 - T_1^4) = F_0 \dot{Q}_H \\ = F_0 A_0 [(\phi_2 + V + 2k_B T_1/q) T_1^2 \exp\left(-\frac{q\phi_2 + qV}{k_B T_1}\right) - \\ (\phi_2 + V + 2k_B T_2/q) T_2^2 \exp\left(-\frac{q\phi_2}{k_B T_2}\right)] + \\ \mu \sigma F_0 (T_1^4 - T_2^4) \quad (10)$$

$$Q_{C,II} = K_2 (T_2^4 - T_3^4) = F_0 \dot{Q}_C \\ = F_0 A_0 [(\phi_2 + 2k_B T_1/q) T_1^2 \exp\left(-\frac{q\phi_2 + qV}{k_B T_1}\right) - \\ (\phi_2 + 2k_B T_2/q) T_2^2 \exp\left(-\frac{q\phi_2}{k_B T_2}\right)] + \\ \mu \sigma F_0 (T_1^4 - T_2^4) \quad (11)$$

In Eqs. (10) and (11), F_0 is the active area of each electrode, i.e., the area facing the interelectrode space.

2.2. Heat flow in thermoelectric part

The thermoelectric part of the combined system is composed of n pairs of thermoelectric elements. Each element is composed a P-type and a N-type semiconductor legs. The thermoelectric

power generation part is assumed to be insulated, both electrically and thermally, from its surroundings, except at the junction-reservoir contacts. An electrical current I_{TE} exists in the thermoelectric generating circuit. One can see from Fig. 1 that the hot thermoelectric junction exchanges heat with the collector while the cold thermoelectric junction exchanges heat with the heat sink. The collector of thermionic part is supplying heat and serving as heat source for the thermoelectric generator. It is obvious that the relation $T_2 > T_3 > T_4 > T_C$ holds for the entire device. Finite rate heat transfers cause the external irreversibilities.

Both the model in Xuan and Li (2003) and the model in the present paper have a thermoelectric power generation module. However, there exists a notable difference between the two models: the thermoelectric module in Xuan and Li (2003) is a single-element generator while the thermoelectric module in the present paper is a multi-element one. Due to its higher efficiency of energy conversion, multi-element power thermoelectric generation modules are usually used for manufacturing the practical thermoelectric devices. Thus, the model of the combined device in the present paper is more practical than that in Xuan and Li (2003).

Assuming that the heat transfer between the hot junction and the collector as well as the heat transfer between the cold junction and the heat sink obey radiative heat transfer law, the heat flow rate entering the hot side ($Q_{H,TE}$) and that leaving the cold side ($Q_{C,TE}$) are defined by Eqs. (12 and 13):

$$Q_{H,TE} = K_3(T_2^4 - T_3^4) \quad (12)$$

$$Q_{C,TE} = K_4(T_4^4 - T_C^4) \quad (13)$$

In Eqs. (12) and (13), K_3 and K_4 are the heat conductances of the heat exchangers between the hot and cold junctions and their respective heat reservoirs.

In the present analysis, three kinds of heat flows are considered inside the thermoelectric part: the first is the heat flow arising from the Seebeck effect; the second is Joule heat of the semiconductor couple, $I_{TE}^2 R$, where R is the total internal electrical resistance of the semiconductor couple; and the last is the conducting heat of the semiconductor couple between the hot and cold junctions, $K_{TE}(T_3 - T_4)$, where K_{TE} is the thermal conductance of the semiconductor couple. The additional heat flow due to heat conduction and Joule heating for the electrical leads connecting the two junctions is ignored in the present model for simplicity. The thermoelectric generating elements are connected in series. The balance equations of heat flow for thermoelectric part are defined by Eqs. (14 and 15):

$$Q_{H,TE} = K_3(T_2^4 - T_3^4) \quad (14)$$

$$= [\alpha T_3 I_{TE} + K_{TE}(T_3 - T_4) - 0.5 I_{TE}^2 R] n$$

$$Q_{C,TE} = K_4(T_4^4 - T_C^4) \quad (15)$$

$$= [\alpha T_4 I_{TE} + K_{TE}(T_3 - T_4) + 0.5 I_{TE}^2 R] n$$

In Eqs. (14) and (15), $\alpha = \alpha_p - \alpha_N$, α_p and α_N are the Seebeck coefficients of the P-type and N-type semiconductor legs; n is the total number of thermoelectric elements.

3. Performance analyses for the combined generator

The thermionic and thermoelectric parts are thermally connected with each other. Thus, the power output of the combined device is given by Eq. (16):

$$P = (Q_{H,TE} - Q_{C,TE}) + (Q_{H,TI} - Q_{C,TI}) \quad (16)$$

$$= F_0 I_{TI} V + [\alpha I_{TE}(T_3 - T_4) - I_{TE}^2 R] n$$

The efficiency the combined system is given by Eq. (17):

$$\eta = P / Q_{H,TI} \quad (17)$$

$$= \{F_0 I_{TI} V + [\alpha I_{TE}(T_3 - T_4) - I_{TE}^2 R] n\} / Q_{H,TI}$$

Theoretically, combining Eqs. (10) with (11) and eliminating the parameters T_1 and T_2 , combining Eqs. (15) with (14) and eliminating the parameters T_3 and T_4 , one can obtain the analytical expressions for the power output and efficiency of the combined device. However, because of the strong nonlinearity, these equations can not be solved analytically and must be solved numerically. For given values of α , ϕ_2 , K_{TE} , K_1 , K_2 , K_3 , K_4 , R , T_H and T_L , the values of T_1 , T_2 , T_3 and T_4 can be solved out for different output voltage V . Then, substituting the values of T_1 , T_2 , T_3 and T_4 into Eqs. (16) and (17) yields the corresponding values of power output and efficiency.

Numerical calculations are performed to analyze the performance of the irreversible combined thermionic-thermoelectric generator. In the calculations, $n = 10$, $\alpha = 2.1 \times 10^{-4} V/K$, $K_{TE} = 1.6 \times 10^{-2} W/K$ and $R = 1.2 \times 10^{-3} \Omega$ are set for the thermoelectric part (Chen et al., 2002); $F_0 = 2.5 \times 10^{-4} m^2$ and the work function $\phi_2 = 1.5V$ which are attainable for practical electrode materials are adopted for the thermionic part (Hatsopoulos and Gyftopoulos, 1973); $T_H = 1500K$, $T_C = 450K$, $K_1 = K_2 = 0.5 \times 10^{-9} W/K^4$ and $K_3 = K_4 = 0.5 \times 10^{-9} W/K^4$ are set for the heat reservoirs and the external heat transfer processes (Janna, 2000). The technique for analysis and the parameters used by Xuan and Li (2003) were for the typical single-element thermoelectric power generation module. While for the multi-element thermoelectric generator, it is more reasonable and accurate to use the

parameters given in Chen et al. (2002) to analyze the performance of the device. In the calculations, the electrode output voltage V in the thermionic part and the working current I_{TE} in the thermoelectric part are taken as the control parameters, which is similar to the analysis process for independent thermionic (Chen et al., 2010; Hatsopoulos and Gyftopoulos, 1973; Mahan, 1994) or thermoelectric device (Chen et al., 2001, 2002, 2005b, 2007; Meng et al., 2011).

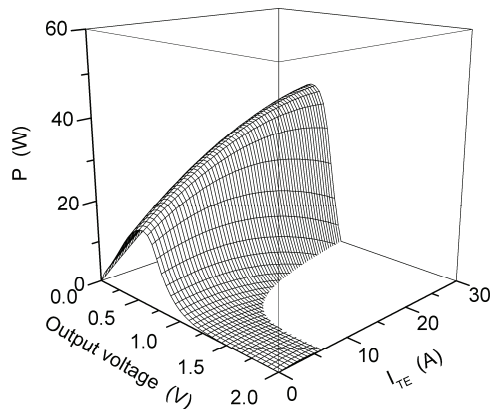


Fig. 2. Power output (P) versus output voltage (V) and working electrical current (I_{TE}) characteristic

By using Eq. (16), a three-dimensional characteristic of power output (P) versus output voltage (V) and working electrical current (I_{TE}) is plotted as shown in Fig. 2. One can see that for fixed V , P is a monotonic function of I_{TE} ; while for fixed I_{TE} , P first increases and then decreases as V increases. There exists an optimal V at which the power reaches the local maximum for a fixed set of design parameters.

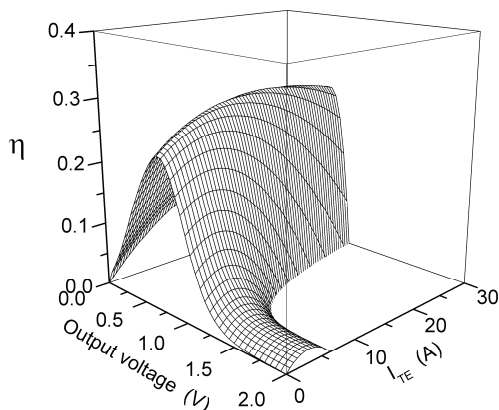


Fig. 3. Efficiency (η) versus output voltage (V) and working electrical current (I_{TE}) characteristic

Similarly, by using Eq. (17), a three-dimensional characteristic of efficiency (η) versus output voltage (V) and working electrical current

(I_{TE}) is plotted as shown in Fig. 3. One can see that the efficiency (η) first increases and then decreases as I_{TE} or V increases. For the fixed design parameters, there exist a pair of optimum I_{TE} and V at which the efficiency attains its local maximum.

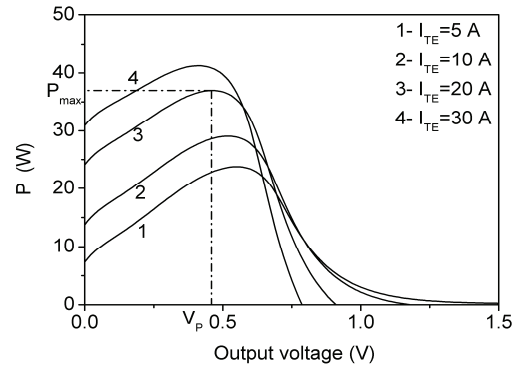


Fig. 4. Effect of working electrical current (I_{TE}) on power output (P) versus output voltage (V) characteristic

The effects of the working electrical current (I_{TE}) on the power output (P) and efficiency (η) characteristics are shown in Figs. 4 and 5. One can see that for fixed I_{TE} , the performance characteristics of P and η versus V are all parabolic-like curves. There exist optimum output voltages (V_p and V_η) which lead to the maximum power output (P_{max}) and maximum efficiency (η_{max}), respectively.

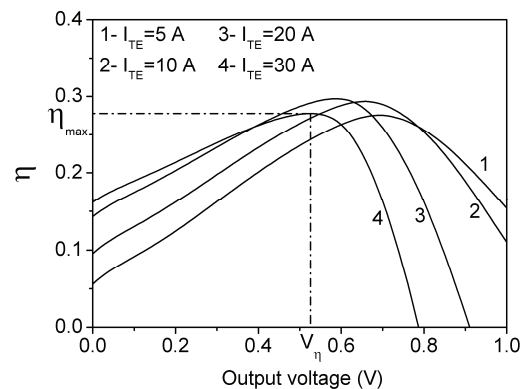


Fig. 5. Effect of working electrical current (I_{TE}) on efficiency (η) versus output voltage (V) characteristic

One can further see that the optimum output voltages (V_p and V_η) decrease as I_{TE} increases; P_{max} increases monotonically while η_{max} first increases and then decreases as I_{TE} increases. For an independent thermoelectric generator, the efficiency will first increase and then decrease with the increase in I_{TE} (Chen et al., 2002, 2005b).

In the design and operation of the combined generator, if one needs to obtain higher power output, the working electrical current I_{TE} should be larger; if

one needs to obtain higher efficiency, I_{TE} should be tuned to its optimal value which lead to the maximum efficiency. In practical application, the value of I_{TE} must be properly chosen in order to obtain the compromise between maximum power and maximum efficiency.

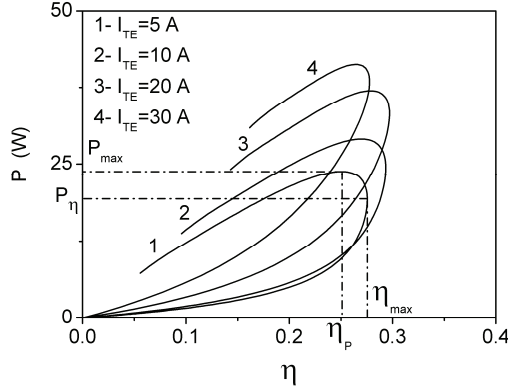


Fig. 6. Effect of the working electrical current (I_{TE}) on power output (P) versus efficiency (η) characteristic

The characteristic curves of power output (P) versus efficiency (η) are shown in Fig. 6. The curves of P versus η are all open loop-shaped ones which are similar to the characteristics of conventional heat engines (Chen et al., 2005b; Chen et al., 1999), and there exist two important points: the maximum power point (η_p, P_{max}) and the maximum efficiency point (η_{max}, P_η). P_η will increase with the increase of I_{TE} while η_p will first increase and then decrease as I_{TE} increases. The optimum regions of power output and efficiency for the combined generator should be $P_\eta < P < P_{max}$ and $\eta_p < \eta < \eta_{max}$.

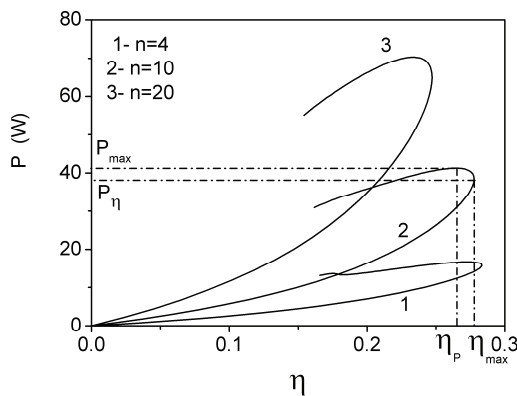


Fig. 7. Effect of the number of thermoelectric generating elements (n) on power output (P) versus efficiency (η) characteristic for a fixed set of parameters

Fig. 7 shows the effect of the number of thermoelectric generating elements (n) on the power output (P) versus efficiency (η) characteristic for a fixed set of parameters. In the practical application of

thermoelectric devices, as the number of thermoelectric generating elements (n) changes, two feasible measures should be taken to rebuild the entire thermoelectric module: one is that the geometry of the entire thermoelectric module and the heat conductance of the two junctions stay unchanged while the geometry, electrical resistance and thermal conductance of the internal thermoelectric element vary with the change of n ; the other is that the geometry of the entire thermoelectric module and the heat conductance of the two junctions vary with n while the geometry, electrical resistance and thermal conductance of the internal thermoelectric element stay unchanged. Considering the structure of the combined device, the high operating temperatures of thermionic generator and the manufacture technics of manufacturing micro energy conversion devices, it's better to use the second project when making such a combined generator. Thus, in the present analyses, the effect of n is discussed by assuming that the geometry and parameters of internal thermoelectric element stay unchanged while the heat conductance of hot and cold junctions vary linearly as n changes.

One can see from Fig. 7 that the maximum power output (P_{max}) increases whereas the maximum efficiency (η_{max}) decreases with the increase of n ; while the values of P_η increases whereas η_p decreases with the increase of n . The reasons for the changes of P_{max} and η_{max} are that: for the maximum power output, as n increases, the values of T_1 , T_2 and T_3 will increase while T_4 will decrease, which will lead to the increase in the power output of the thermionic part and the thermoelectric part; while for the maximum efficiency, as n increases, the internal dissipation in the thermoelectric part, such as Joule heat and conducting heat will increase, thus the overall efficiency of the combined device will decrease. It should be noted that achieving high power output by applying a large number of thermoelectric generating elements (n) yields low efficiency. In practice, if higher power output is expected for the combined device, the device needs more thermoelectric generating elements; if higher efficiency is expected for the combined device, the device needs fewer thermoelectric generating elements. Therefore, when choosing the value of n , a trade-off must take to ensure reasonable power output and efficiency.

Figs. 8 and 9 show the effect of heat sink temperature (T_c) on the power output (P) versus electrical current density (I_{TI}) and efficiency (η) versus electrical current density (I_{TI}) characteristics.

The characteristic curves of power output and efficiency versus I_{TI} are all parabolic-like ones. There exist an optimum electrical current density ($I_{TI,P}$) which leads to the maximum power output (P_{max}) as well as an optimum electrical current

density ($I_{Tl,\eta}$) which leads to the maximum efficiency (η_{max}). The maximum power output (P_{max}), the maximum efficiency (η_{max}) and the optimum electrical current density ($I_{Tl,P}$ and $I_{Tl,\eta}$) decrease as T_C increases. Practically, the temperature of heat sink should be as low as possible in order to increase the power and efficiency of the combined generator.

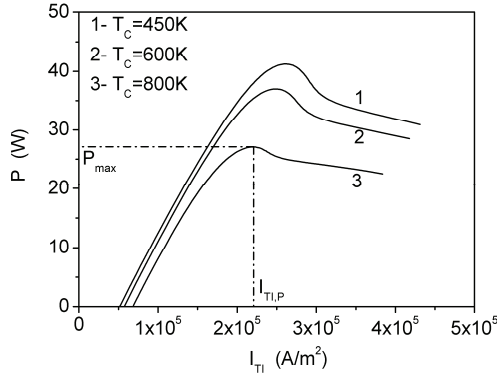


Fig. 8. Effect of heat sink temperature (T_C) on the power output (P) versus output voltage (V) characteristic

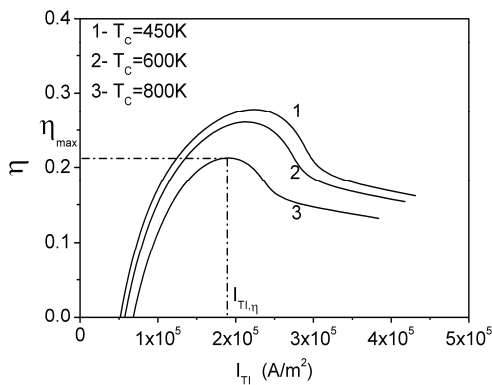


Fig. 9. Effect of heat sink temperature (T_C) on efficiency (η) versus the output voltage (V) characteristic

Fig. 10 shows the temperature difference ($\Delta T = T_1 - T_2$) of the thermionic electrodes versus the output voltage (V) characteristic for different collector work functions. In traditional non-equilibrium thermodynamic analyses, no finite rate heat transfer is considered for each electrode and the temperature of the electrode is a constant; while in the present analysis, finite rate heat transfer between the electrode and the heat reservoir is taken into account, thus the temperatures of the electrodes are no longer the same as those of the heat reservoirs, which leads to the change of temperature difference ΔT . The temperature difference increases with the increase of V . As the work function increases, the slope of the curve becomes steeper; for fixed output voltage, larger collector work function corresponds to higher electrode temperature difference. However, as V increases, the temperature differences with

different work function tend to saturate at the same maximum temperature difference. Actually, stable metal material with low enough work function is a key factor which determines the development of thermionic power generator. In the combined generator, materials with low work functions are also needed in order to lower the working temperature and improve the efficiency of the combined device.

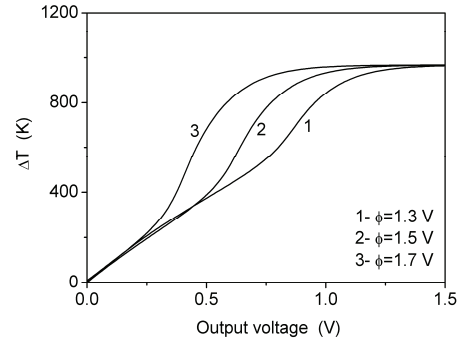


Fig. 10. Temperature difference (ΔT) of the thermionic electrodes versus the output voltage (V) characteristic

4. Special cases and performance comparisons

4.1. Special cases

It is worth pointing out that based on the irreversible combined thermionic-thermoelectric generator model with finite rate heat transfer, some important results in previous analyses (Houston, 1959; Rasor, 1960; Wilson, 1959; Xuan and Li, 2003) can be directly derived from the limit cases in the present paper. If the internal and external finite rate heat transfer processes in the combined device are ignored, then $k_1 F_1 = k_2 F_2 \rightarrow \infty$ and $k_3 F_3 = k_4 F_4 \rightarrow \infty$, which lead to $T_1 = T_H$, $T_3 = T_2$ and $T_4 = T_C$. In these conditions, Eqs. (3)-(17) become the results of traditional non-equilibrium thermodynamic analysis. The corresponding electrical current density (I_{Tl}^i) in the thermionic part can be derived from Eq. (4) (Eq. 18):

$$I_{Tl}^i = A_0 [T_H^2 \exp(-\frac{q\phi_2 + qV}{k_B T_H}) - T_C^2 \exp(-\frac{q\phi_2}{k_B T_C})] \quad (18)$$

The total heat ($Q_{H,Tl}^i$) leaving the emitter is given by Eq. (19):

$$Q_{H,Tl}^i = F_0 A_0 [(\phi_2 + V + 2k_B T_H / q) T_H^2 \exp(-\frac{q\phi_2 + qV}{k_B T_H}) - (\phi_2 + V + 2k_B T_C / q) T_C^2 \exp(-\frac{q\phi_2}{k_B T_C})] + \mu \sigma F_0 (T_H^4 - T_C^4) \quad (19)$$

The corresponding power output (P^i) and efficiency (η^i) are given by Eqs. (20 and 21):

$$P^i = F_0 I_{Tl}^i V + [I_{TE}^2 R + \alpha I_{TE} (T_2 - T_C)] n \quad (20)$$

$$\eta^i = P^i / Q_{H, TI}^i = \{F_0 I_{TI}^i V + [I_{TE}^2 R + \alpha I_{TE} (T_2 - T_C)] n\} / Q_{H, TI}^i \quad (21)$$

If the values of n is taken to be unity, Eqs. (18)-(21) become the results similar to those obtained by Xuan and Li (2003) for the performances of a combined thermionic-thermoelectric generator without considering finite rate heat transfer.

If the thermoelectric generator in the combined device is further ignored, the whole device can be simplified into an independent thermionic generator considering external heat transfer. In this condition, the two emitter and collector of the thermionic generator exchange heat with the heat source and heat sink, respectively. The electrical current density is given by Eq. (4). And the corresponding power output (P_{TI}) and efficiency (η_{TI}) are given by Eqs. (22 and 23):

$$P_{TI} = F_0 I_{TI} V \quad (22)$$

$$\eta_{TI} = P_{TI} / Q_{H, TI} = F_0 I V / Q_{H, TI} \quad (23)$$

In the above two equations, $Q_{H, TI}$ is the total heat leaving the heat source which is defined by Eq. (10). Eqs. (22)-(23) are expressions for the power output and efficiency performances of an independent thermionic generator considering external finite rate heat transfer.

4.2. Performance comparisons

In the following analysis, numerical examples are provided to show the performance comparisons among the three different generator models, i.e., the irreversible combined thermionic-thermoelectric generator with finite rate heat transfer, the combined thermionic-thermoelectric generator without considering finite rate heat transfer, and the independent thermionic generator considering external finite rate heat transfer.

The performance improvement of combined device is due to the fact that the energy leaving the emitter can be further utilized the thermoelectric part. In the present analysis, the working temperatures of the thermionic electrodes for the combined device are not designated values but derived from the thermionic property and energy balance of the entire system. However, it is worth pointing out that the working temperatures of the independent thermionic device which is used for performance comparison are not the heat reservoir temperatures $T_H = 1500K$ or $T_C = 450K$. The working temperature of the collector of practical thermionic devices usually ranges from $800K$ to $1200K$. In order to compare the performance of the independent thermionic device with that of the combined device, the reservoir temperatures for the independent thermionic generator are taken as the electrode temperatures of

the combined thermionic-thermoelectric generator at which the power output attains its maximum value.

The comparisons of power output versus the output voltage (V) characteristics for the three different generator models are shown in Fig. 11. The power output performance of three different generators all first increase and then decrease as the output voltage increases. The influence of heat transfer irreversibility is quite obvious. One can see that the power output of combined generator is generally reduced by the finite rate heat transfer and P is always lower than P^i . Taking the curves 1 and 2 in Fig. 11 for example, the maximum power output of the combined device decreases by 44.80% once the heat transfer is considered.

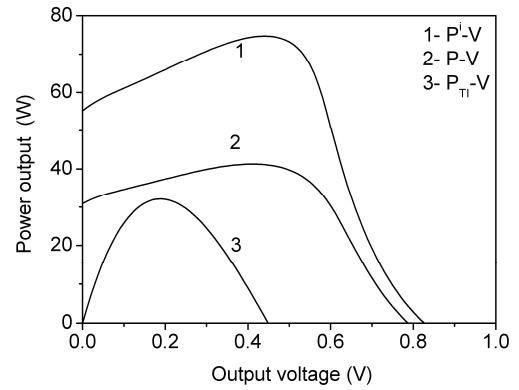


Fig. 11. Comparisons of power output versus the output voltage (V) characteristics for the three different generator models

As expected, the performance improvement due to the Seebeck effect of the thermoelectric elements is significant. For fixed output voltage, the power output (P and P^i) of the combined thermionic-thermoelectric devices are much larger than that (P_{TI}) of the independent thermionic generator. The working temperature of the collector with a work function of $1.5V$ is about $1000K$. For an independent thermionic generator, the amount of heat leaving the collector with such a high temperature is large and this heat is totally released to the cold heat reservoir; while in the combined device, the thermoelectric generator is thermally connected to the collector of the thermionic part and the heat leaving the collector can be further utilized, which increases the overall performance of the entire device. The maximum power output of the irreversible combined device increases by 28.38% when compared with the independent thermionic generator considering external heat transfer, as shown by curves 2 and 3 in Fig. 11.

The efficiency performance comparisons for the three different generator models are shown in Fig. 12. The efficiency always first increases and then decreases as V increases. The overall efficiency performance of the combined generator is reduced by the external heat transfer and η is always smaller

than η^i . The maximum efficiency of the combined device decreases by 21.35% if the heat transfer is taken into account, as shown by curves 1 and 2 in Fig. 12. For fixed V , the efficiency of combined device (η or η^i) is much larger than that (η_{Ti}) of the independent thermionic generator. The maximum efficiency of the irreversible combined device increases by 89.57% when compared with the independent irreversible thermionic generator, as shown by curves 2 and 3 in Fig. 12.

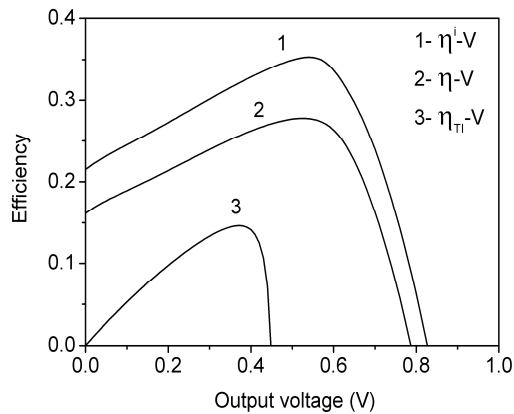


Fig. 12. Efficiency performance comparisons for three different generator models

Comparisons of power versus efficiency performance characteristic for the generator models are further shown in Fig. 13. One can see that the power versus efficiency characteristic curves ($P-\eta$ and $P^i-\eta^i$) of the combined generators are open loop-shaped ones; while the characteristic curves ($P_{Ti}-\eta_{Ti}$) of the independent thermionic generators is a closed loop-shaped one. For a given power output, the efficiencies of the combined generators are much larger than that of the independent thermionic generator.

The qualitative difference of power versus efficiency performance characteristic between the combined generator and the independent thermionic generator is caused by the Seebeck effect of the thermoelectric module. For an independent thermionic generator, there exists the internal radiative heat transfer between the electrodes and the power versus efficiency characteristic curves are closed loop-shaped ones, which are similar to those of the conventional steady flow heat engines with direct heat leakage between two heat reservoirs (Andresen, 1983; Bejan, 1996; Chen et al., 1999). While for the combined generator, a thermoelectric generator is coupled to the collector of the thermionic generator to further utilize the emitted heat. The collector is served as the heat source of the thermoelectric module.

Due to the high working temperature of thermionic generator, even before the thermionic generator itself begins to work, the temperature of the

collector is high enough to power the thermoelectric generator. In other words, the thermoelectric generator starts up and generates power ahead of the thermionic generator in the combined device, and there exists power output when the combined generator starts to work. Thus both power and efficiency at the start point of the characteristic curves for the combined device are nonzero. One can conclude that it is the coupled thermoelectric generator which leads to the difference in performance characteristics for the two kinds of devices.

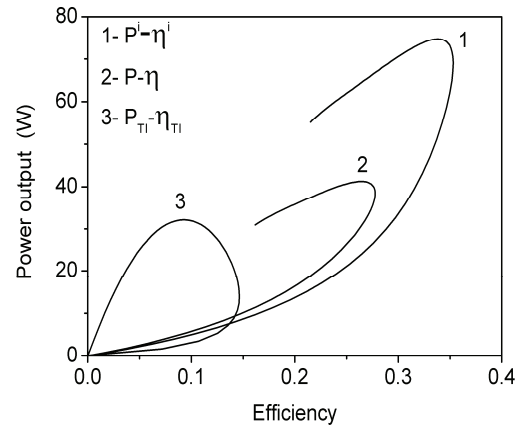


Fig. 13. Comparisons of power output versus efficiency characteristics for the three different generator models.

Results of above performance comparison and analysis have shown that the finite rate heat transfer processes have great influences on the performance of the combined generator. The obtained results may provide guidelines for the design and application of practical solar-powered combined thermionic-thermoelectric generators. When constructing such a solar-driven combined converter, the heat transfer between the solar energy collector and the emitter of the thermionic generator and that between the cold junction of the thermoelectric generator and the heat sink are important factors that must be taken into account.

5. Conclusions

The optimal performance of an irreversible combined thermionic-thermoelectric generator is studied. The characteristic curves of power versus efficiency are open loop-shaped ones, and the design parameters such as working current of the thermoelectric circuit have great influences on the device performance. In practical design and operation, the design parameters should be properly chosen in order to obtain the compromise between maximum power and maximum efficiency. The power and efficiency of the combined device are obviously reduced by the heat transfer losses. The performance of the combined generator is generally superior to that of an independent vacuum thermionic generator.

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SUBSTRATE INHIBITION KINETICS OF MALATHION BIODEGRADATION AND THE EFFECT OF MOLASSES AS COSUBSTRATE

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Abstract

Malathion is a toxic, wide-spectrum organophosphorus pesticide. The removal of this pesticide from water is one of the major environmental concerns. In this study, the biodegradation of malathion using batch activated sludge was studied. The effect of initial malathion concentration (5 to 140 mg/L) on the degradation process was investigated. The biokinetic parameters ($r_{s\max}$, K_s and K_i) were estimated. Identification of dominant bacterial flora was also achieved. In addition, two kinds of additional carbon sources, i.e., glucose, and molasses (5000 mg/L) were tested to choose a favourite carbon source for malathion cometabolism of activated sludge. Metabolites resulting from biodegradation were also investigated. Results showed that local activated sludge used in this study could effectively degrade malathion. There was a decrease in specific substrate consumption rate at initial malathion concentration of 120 mg/L due to inhibitory effect of the pesticide on its own degradation with $K_i = 192$ mg/L. In the presence of molasses at 5000 mg/L used as cosubstrate, 92% of the initial dose of insecticide (60 mg/L) was degraded within 75 h. Results from GC-MS analysis revealed that malathion monocarboxylic acid was the major degrading compound.

Key words: activated sludge, degradation, inhibition, malathion, molasses

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1. Introduction

Increasing demand for water, driven by both population growth and urban expansion, forces water agencies to seriously evaluate new water reuse systems and technologies for alternative water resource options. Current and future demand for water cannot be fully achieved by traditional hydrological cycle-dependent water resources, therefore purified wastewater has to be reclaimed and recycled (Graczyk et al., 2009).

At the present time, the most widely used pesticides belong to the organophosphorus group. These pesticides are an important source of environmental contamination owing to their widespread use in agriculture; this involves their later

passage to the fruit with the ensuing risk for the population. In addition, organophosphorus were known to reduce the activity of neurotransmitters and hence to cause irreversible effects on the nervous system (Zhao et al., 2011). Malathion S-[1, 2-di(ethoxycarbonyl) ethyl] dimethyl phosphorothiolothionate; CAS No 121-75-5; $C_{10}H_{19}O_6PS_2$] is one of the most widely used organophosphate insecticides throughout the world because of its efficacious insects control. Indeed, malathion is commonly used to control mosquitos and variety of insects that attack fruits, vegetables landscaping plants and shrubs (WHO, 2004). Malathion is slightly toxic compound and it is classified as a toxicity class III pesticide by the U.S. Environmental Protection Agency, EPA (Zheng and

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Hwang, 2006). The goal of remediation effort is to limit the extent of contamination at a hazardous waste site, to prevent further deterioration of the environment and to prevent exposure by humans and other life forms to hazardous chemicals (Pavel and Gavrilescu, 2008).

Because of the problems associated with pollutant treatment by conventional methods, such as incineration or landfill, increasing consideration has been placed on the development of alternative, economical and reliable biological treatments (Chen et al., 1999).

Microbial degradation is considered to be a major factor determining the fate of organophosphorus insecticides in environment (Hayatsu et al., 2000). Nevertheless, in some cases, biotransformation reactions generate products that have similar or greater levels of toxicity than those of the parent contaminant (Becker and Seagren, 2010). The majority of studies regarding the biodegradation of malathion have been performed using pure cultures (Abraham and Srujana, 2014; Jilani, 2013; Mohamed et al., 2010; Sabit et al., 2011), and a few studies have focused on malathion biodegradation by activated sludge culture. Activated sludge process, which is a biological wastewater treatment method is mostly used in the world for treating sewage (Li et al., 2009).

In activated sludge process, evaluation of the inhibitory effect of toxic substrates on biological mass becomes a major consideration (Hao et al., 2002). The evaluation of such inhibitory effect can be performed by mathematical modelling approach. In this study, the Haldane model, developed to describe the biological treatment processes considering inhibitory conditions, was applied (Eq. 1):

Haldane equation (Edwards, 1970):

$$r_s = r_{s \max} S K_i / (K_s + S) (S + K_i) \quad (1)$$

where: K_s , K_i , r_s , $r_{s \max}$ and S are half saturation constant (mg/L), inhibition constant (mg/L), specific substrate consumption rate (1/h), maximum specific substrate consumption rate (1/h) and substrate concentration (mg/L), respectively.

The specific substrate consumption rate decreases when a maximum tolerable substrate concentration is exceeded. The inhibition constant K_i is the substrate concentration, where substrate degradation is reduced to 50% of the maximum specific substrate consumption rate due to substrate inhibition.

A number of organic compounds, including, sodium succinate, sodium acetate, glucose, ethanol and fructose, have been tested as primary carbon sources to enhance cometabolism degradation of malathion, but, few publications have been reported on the utilization of molasses as cosubstrate in the treatment of hazardous contaminants: 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (Kao et al., 2001) and pentachlorophenol (Kao et al., 2004).

To the best of our knowledge, no work has been published neither on the estimation of biokinetic constants inherent to the inhibitory effect of malathion on both its own transformation or on the growth inhibition kinetics of microorganisms, nor on the degradation of malathion in the presence of molasses as cosubstrate.

Therefore, the aim of this study is to investigate the effect of initial malathion concentration on the degradation potential of activated sludge culture. The Haldane substrate inhibition was used to model the inhibition effect of malathion on its own degradation and the kinetic constants were evaluated. The feasibility of using glucose and molasses; which is known as waste product from sugar industry; as a growth substrate for cometabolic transformation of malathion using acclimated activated sludge culture was also investigated. Identification and enumeration of dominant aerobic, heterotrophic bacteria of activated sludge used in this study were also achieved.

2. Material and methods

2.1. Microorganisms

In this study, the investigations were carried out using a mixed activated sludge, which was collected from the aeration basin of wastewater treatment plant situated in Ain Benian, Algiers. The activated sludge culture was carried out in a aeration tank (9L) using the mineral salt medium described below supplemented with 5000 mg/L glucose used as the sole source of carbon.

2.2. Cultivation media

The composition of the mineral salt medium used was as follows (g/L): 0.1g K₂HPO₄, 0.2g MgSO₄, 0.001g FeSO₄, 1.0g (NH₄)₂SO₄, 1.0g NaCl, and 0.0033g NaMoO₄ (Barik et al., 1984). Technical grade malathion of 95% purity was purchased from Alphyte Co., Algeria. Malathion was dissolved in 0.5 ml ethanol (purity > 99%) before being added to the mineral salt medium. The investigation of the influence of additional carbon sources on malathion biodegradation was carried out by adding separately 5000 mg/L glucose or clarified molasses to the mineral salt medium in the presence of malathion at 60 mg/L.

2.3. Malathion biodegradation

2.3.1. Treatment of malathion used as the sole carbon and energy sources

The culture experiments were realized in 1000 mL Erlenmeyer flasks containing 250 mL of the mineral salt medium. The flasks were inoculated with 250 mL activated sludge culture at 4000 mg/L biomass. Malathion was tested at different concentrations ranging from 5 mg/L to 140 mg/L.

All cultures were grown aerobically and were kept on a magnetic stirrer at 200 rpm and ambient temperature (25°C, max. deviation $\pm 2^\circ\text{C}$). The final pH of the media was adjusted to 6.0 by using 1.0 mol/L sodium hydroxide and 0.5 mol/L sulphuric acid solutions.

All culture flasks were covered with aluminium foil to protect malathion from degradation by ultraviolet irradiations.

2.4. Analytical techniques

2.4.1. Dominant bacterial flora study

Colilert[®]-18 (IDEXX Laboratories) test which is approved by **U.S. Environmental Protection Agency** and included in Standard Methods for Examination of Water and Wastewater and Enterolert[™]-E (IDEXX Laboratories) test which correlates with the European Bathing Water Directive standard method for enterococci, were used for the identification and the enumeration of coliforms and enterococci, respectively. For the determination of numbers of *Pseudomonas aeruginosa* and Sulfitorreductor bacteria and their identification, the membrane filter technique was used, according to NF EN 12780 and ISO 6461-2, respectively. *Salmonella* was investigated according to the method recommended by Standing Committee of Analysts (2006). For the identification and the enumeration of coagulase-positive Staphylococci, selective medium of Chapman was used according to the formulation given by Marchal et al. (1982). Both catalase and coagulase tests were performed for confirmation.

2.4.2. Estimation of biomass concentration

The determination of biomass concentrations were carried out by measuring mixed liquor volatile suspended solids (MLVSS) concentrations. A calibration curve was established by plotting absorbance red at a wavelength of 550 nm with a UV-Vis spectrophotometer (Shimadzu, UV mini 1240) versus MLVSS.

2.4.3. Estimation of malathion concentration

Samples were withdrawn at various time intervals and filtered through a 0.45 μm pore size membrane filter. Filtrate malathion concentrations were carried out on clear supernatant using colorimetric method proposed by Naidu et al. (1990). Absorbance at 825 nm is measured using UV-Vis spectrophotometer (Shimadzu, UV mini-1240).

2.4.4. Kinetic tests

The exponential phase was used to determine the specific growth rate μ_x (1/h) values from data according to the following formula (Eq. 2):

$$\ln (X/X_0) = \mu_x t \quad (2)$$

where X_0 is the concentration of cells at time zero and X is the concentration of cells at time t .

On the other hand, specific rate of substrate consumption r_s (1/h) was also calculated according to the following equation (Eq. 3):

$$r_s = - dS/(dt X) \quad (3)$$

where X and S represent the concentration of cells and the concentration of substrate, respectively at time t .

In the present study, the Haldane kinetic model (Edwards, 1970), based on the specific rate of substrate assimilation, was used to fit the experimental batch data obtained for the activated sludge culture with malathion concentrations ranging from 5 mg/L to 140 mg/L. Statistica Release 7.0 software (StatSoft Inc.) was used to solve the model equation using nonlinear regression method.

2.4.5. Analysis of malathion - derived degradation products

Residual malathion and malathion breakdown products extracted from the microbial degradation study, according to Kaur et al. (1997) method, were identified by GC-MS method. Gas chromatography was performed using a HP6800 plus gas chromatograph equipped with an analytical capillary column (HP-5 MS coated with 5% diphenyl-95% dimethylpolysiloxane [30m x 0.25mm i.d. x 0.32 μm film thickness]).

Helium was used as the carrier gas at flow rate of 1ml min⁻¹. Temperature at injection port was 250°C. Injection volume of 1 μl was used (splitless injection). The column temperature was programmed from 90°C to 250°C at 10°C.min⁻¹; run time, 15 min. For the mass spectrometric detection, HP 5973 Mass Selective Detector has been used.

A potential of 70 eV has been imposed. The ion source was maintained at 200 °C and the analysis was performed by the selected ion monitoring (SIM) mode. GC-MS interface was 280 °C. Compounds were identified using Agilent MSD ChemStation software.

2.4.6. Statistical analysis

All experimental measurements were carried out in duplicate. Statistical analysis was performed using Student's t test. P values < 0.05 were considered statistically significant.

3. Results and discussion

3.1. Microbial counts

Activated sludge was sampled for microbiological assay after treatment with malathion (60 mg/L) used as the sole carbon source. The results obtained are recorded in table1. It is interesting to note that Enterococci constituted the main microflora (65%). *Pseudomonas aeruginosa* constitute 12% of the sludge flora. However, Coliforms constitute less than 0.7% of the sludge flora. On the other hand, sulfite-reducing clostridia (7%) which are anaerobic

bacteria, and therefore, present in the shape of spores, should not involve in malathion removal in this study, because the treatment is based on aerobic activated sludge. The numbers of *Salmonella* and coagulase-negative *Staphylococcus* were accounted for 8% and 7% of the total viable population, respectively. At last, it should be pointed out that relatively few fungi were identified from activated sludge. The direct sampling onto agar plates of sample gave only one colony identified as *Penicillium sp.*

Table 1. Numbers of dominant microflora

Coliforms (MPN^a/mL)	4,010
Enterococci (MPN/mL)	401,000
Coagulase-negative Staphylococcus (CFU^b/mL)	45,000
Sulfite-reducing clostridia (CFU/mL)	42,000
Salmonella (CFU/mL)	52,000
Pseudomonas aeruginosa (CFU/mL)	72,000
Penicillium sp. (CFU/mL)	1

^a(Most Probable Number), ^b(Colony-forming Unit)

The results obtained revealed that activated sludge used in this study had a preponderance of enterococci population. Among the several bacteria isolated from different biota that were able to degrade malathion, there have been no reports showing the degradation of this pesticide by enterococci bacteria. This observation merits further study, and might lead to demonstrate the ability of enterococci to degrade malathion. In addition, *Pseudomonas aeruginosa*, which was one of the most predominant bacteria found in the activated sludge used in this study, could be involved in malathion degradation. In fact, according to literature, many strains of *pseudomonas* species are known to metabolize malathion (Abraham and Srujana, 2014; Barik et al., 1984; Goda et al., 2010; Jilani, 2013).

3.2. Effect of initial malathion concentration on its own biodegradation

Eight batch cultivation experiments were carried out using an initial biomass concentration of 2000 mg/L grown on the malathion as sole source of carbon and energy. The initial malathion concentrations in the medium ranged from 5 to 140 mg/L. The extent of malathion degradation was investigated. Variation of malathion concentration against time is shown in Fig. 1, at various initial pesticide concentrations. Results show that the mixed culture tested was able to degrade the pesticide under a range of conditions in liquid culture. As can be seen from the figure, complete removal of malathion was not achieved at all concentrations studied. It could be seen from the figure that the degradation of the pesticide did not start directly. It was observed a transition period before the onset of detectable microbial degradation. After this period, malathion is depleted more quickly. Possible explanation is that before microbial cells can start active metabolism of

malathion, they have to adjust to their new surrounding environment before exponentially growing. This period is referred to as the lag phase and can take several hours (18-55h in this study), in which the enzymes involved in malathion catabolism would be reactivated or expressed. During the lag phase, the number of individual cells remains approximately constant or increases slowly (Prats et al., 2008). Moreover, the concentration of the pesticide seems to have an effect on this duration since the later was observed to be longer (55h) when malathion concentration is higher (140 mg/L). This could be due to the malathion-inhibition effect for microbial mixed culture occurs at such high concentration, suggesting that at high malathion concentrations previous exposure to a malathion-containing environment is not enough to enable the cell mass in activated sludge to resist to the toxic effects of malathion.

The maxima percentages of malathion degradation obtained for different initial malathion concentrations at the end of degradation and the time taken to reach them are shown in Table 2. It is clear from the Table that malathion was not completely degraded and the time taken by the mixed culture to reach the maximum percentage of malathion removal was dependent upon its initial concentration. It should be noted, in particular, that a longer time was required to reach the maximum removal of 140 mg/L malathion, possibly due to the toxicity exerted by the pesticide at such concentration. Similar observations have also been reported for the growth of indigenous mixed microbial culture with m-cresol (Saravanan et al., 2009).

On the other hand, the results indicate that the highest malathion removal value was obtained for 60 mg/L malathion corresponding to a removal efficiency of about 77% obtained after 67h of cultivation. This leads to the conclusion that malathion concentration of 60 mg/L may be considered as the optimum malathion concentration for the growth of the mixed culture used in this study.

3.3. Modeling the degradation kinetic of malathion biodegradation

The experimental data on specific malathion degradation rate (r_s) obtained at various initial malathion concentrations were used for estimating the kinetic parameters ($r_{s\ max}$, K_s and K_i) from the model previously described. Fig. 2 shows a comparison between data obtained experimentally at room temperature and pH 6 and the values predicted by Eq. (1). From Fig. 2, it could be seen that for relatively lower concentrations of malathion (5-100 mg/L), the specific malathion consumption rates (r_s) increased with increasing malathion concentration and reached a maximum value of $0.114 \cdot 10^{-2}$ 1/h when the concentration of the pesticide was 100 mg/L. Whereas, when malathion concentration exceeded this threshold value, the r_s dropped drastically to $0.046 \cdot 10^{-2}$ and $0.034 \cdot 10^{-2}$ 1/h for initial malathion

concentrations of 120 and 140 mg/L, respectively as a result of an inhibitory effect.

The kinetic parameters are obtained to be 0.2410^{-2} 1/h, 192 mg/L and 192 mg/L, respectively with determination coefficient $R^2=0.76$. Malathion undergoes chemical hydrolysis in aqueous solutions. The rate of transformation depends heavily on pH of the environmental medium. In fact, Wang (1991) found that in sterilized water, malathion was quite stable under neutral pH conditions and that

susceptibility to hydrolysis increased with increasing alkalinity. In the present study, the pH of the medium was maintained at 6.0 for this purpose.

The present study indicates that activated sludge could utilize malathion as the sole carbon source and energy source. The substrate threshold value (100 mg/L) shows that the mixed bacterial population present in the activated sludge has a high tolerance to malathion.

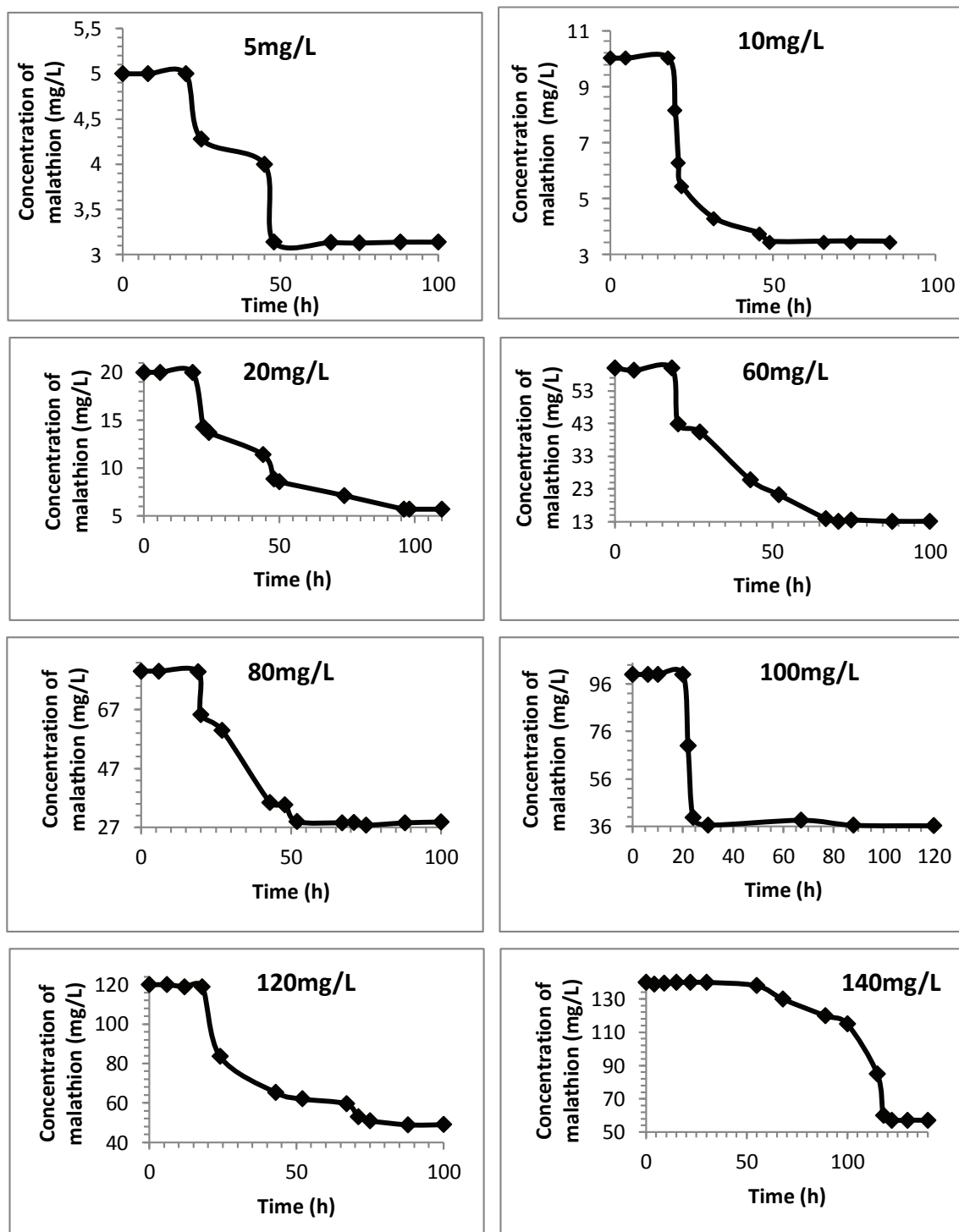
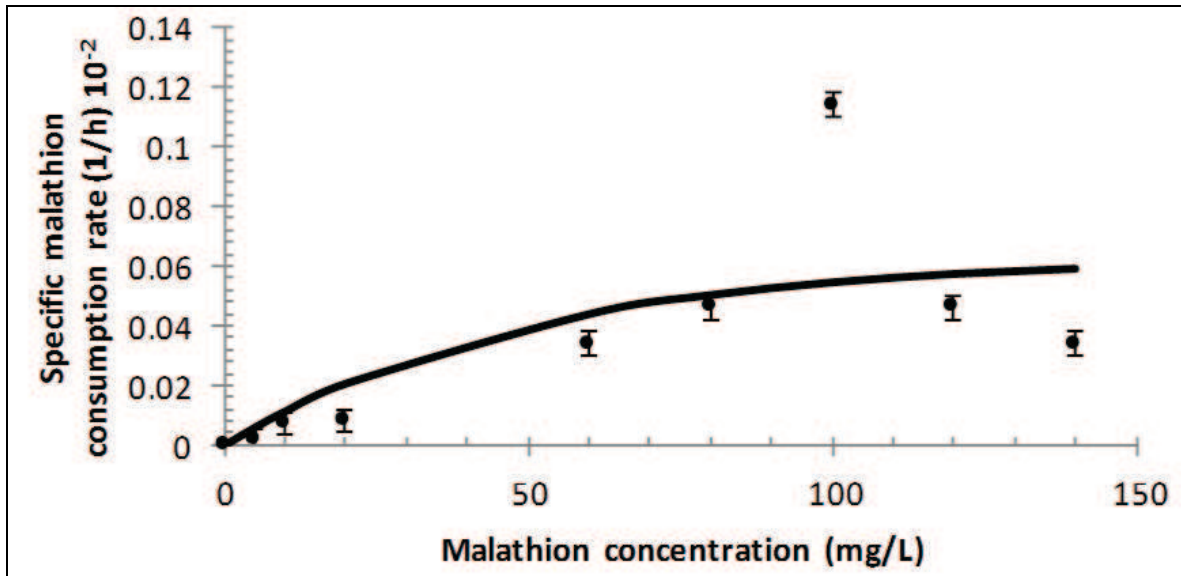


Fig. 1. Effect of initial malathion concentration (5-140 mg/L) on malathion biodegradation (initial cell concentration was 2000 mg/L)

Table 2. Maximum percentages of malathion degradation for its different initial concentrations (5-140 mg/L) and the time taken to reach them

Initial malathion concentration (mg/L)	Maximum malathion degradation (%)	Time required to reach the maximum malathion degradation(h)
5	37	48
10	66	49
20	71	96
60	77	67
80	64	52
100	63	30
120	59	88
140	59	122

**Fig. 2.** Experimental and predicted specific substrate consumption rate at different malathion concentrations due to Haldane model. Markers are experimental data (●). Line is the fit of Haldane equation to the experimental data

The specific malathion degradation rate was found to be low at 120 and 140 mg/L of malathion concentrations. The reason could be that the addition of malathion up to 100 mg/L seemed to inhibit enzymes involved in the different steps of its own degradation. This result agreed with the previous report by Singh and Seth (1989), who studied the biodegradation of malathion by *Pseudomonas sp.* M-3 strain isolated from industrial effluents and found that the rate of degradation of the pesticide in the presence of ethanol was low when it was tested at higher concentration.

In this study, the P value and determination coefficient (R^2) statistic criteria were used. When P values are less than 0.05, this means that the dependent variable may be predicted from independent variable. On the other hand, R^2 value close to 1 means that the equation is a good function which shows a significant relationship between the independent and dependent variables. Observation on P and R^2 values (0.025 and 0.76, respectively) concludes that the kinetic model of the Haldane model could explain the behaviour of the local activated sludge in the removal of malathion. Others kinetic models of substrate inhibition (Aiba, Tseng

and Wayman, Han and Levenspiel, Luong, Edwards, and Teissier) were previously compared in order to find out which one describes the experimental data best (data not shown). It was found that Aiba, Teissier, Edwards, Tseng and Wayman models do not at all fit the experimental data. However, Han-Levenspiel and Luong models gave R^2 values which were less than the R^2 value obtained in the present study.

The R^2 value obtained here that is not very high could be explained by the fact that the model used in the present study is appropriate for homogenous cultures, but not for heterogenous cultures or complex substrates. An other reason could be that in this work, concentrations of malathion higher than 140 mg/L were not tested because of the low solubility of the pesticide in water (145 mg/L at 25° C). The effect of a toxic compound on its biodegradation is estimated by the term K_i . It should be noted that when K_i is very large, it can be said that the inhibition effect can be observed at high substrate concentrations. So, high value of K_i (192 mg/L) obtained in this study indicates that the mixed microbial consortium used has a high resistance of substrate inhibition.

3.3. Effect of glucose and molasses on malathion removal and on growth kinetics

The effect of the presence of organic substrates (glucose and molasses) on the biodegradation of malathion tested at 60 mg/L was investigated. The initial MLVSS concentration was 2000 mg/L. The variation of malathion concentration with time with and without glucose and molasses (5000 mg/L) is shown in Fig. 3. As can be seen from the figure, it appears that in the absence of additional carbon sources, malathion degradation started after 19h of incubation. For the experiments conducted in presence of molasses and glucose, malathion degradation appeared after 28h and 45h of incubation, respectively.

The time required to reach the stationary phase of removal was 71h when malathion was the sole source of carbon and 75h in the presence of both glucose and molasses. Removal efficiency obtained for the control with no additional carbon sources was 78% and reached 84% and 92%, with glucose and molasses, respectively. On the other hand, specific rates of malathion consumption observed were very close: $0.034 \cdot 10^{-2}$ 1/h, for pesticide alone and, $0.03 \cdot 10^{-2}$ 1/h and $0.02 \cdot 10^{-2}$ 1/h for pesticide in the presence of glucose and molasses, respectively. Growth kinetics

experiments were conducted in the presence of additional carbon sources (glucose and molasses) at 5000 mg/L with initial malathion concentration of 60 mg/L. The initial cell concentration expressed through the concentration of MLVSS was 2000 mg/L. Figure 4 shows time-course variation in MLVSS concentration during the batch experiments. The results clearly indicate that addition of carbohydrate sources induced a rapid increase in cell numbers. Indeed, in the presence of glucose and molasses, the specific growth rates (μ_x) calculated from the exponential phase of growth curves ($1.1 \cdot 10^{-3}$ 1/h and $7.5 \cdot 10^{-3}$ 1/h, respectively) were significantly higher than that attained in the presence of malathion used as the sole source of carbon ($2 \cdot 10^{-4}$ 1/h).

The effects of the additional carbon source on co-metabolic process can be summarized in two points: one is to stimulate cell growth and enhance the degradation of the non-growth substrate; the other is to act as a co-substrate in xenobiotic metabolism by inducing certain enzymatic reaction (Xie et al., 2009). Our results show that activated sludge could metabolize malathion and that external carbon sources accelerated cell growth. The addition of molasses significantly promoted the degradation rate of malathion ($p < 0.05$) as compared to the control (without molasses and glucose).

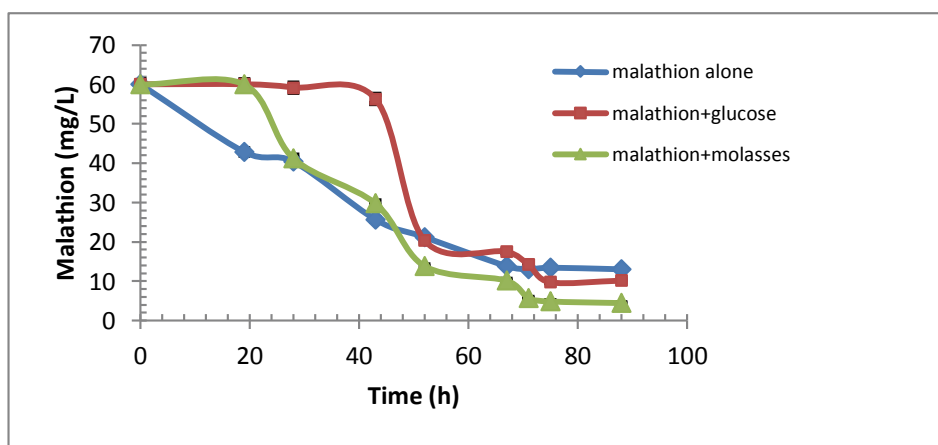


Fig. 3. Variation of malathion concentration as a function of time in the absence or the presence of additional organic substrates (glucose and molasses) tested separately (malathion = 60 mg/L, glucose and molasses = 5000 mg/L)

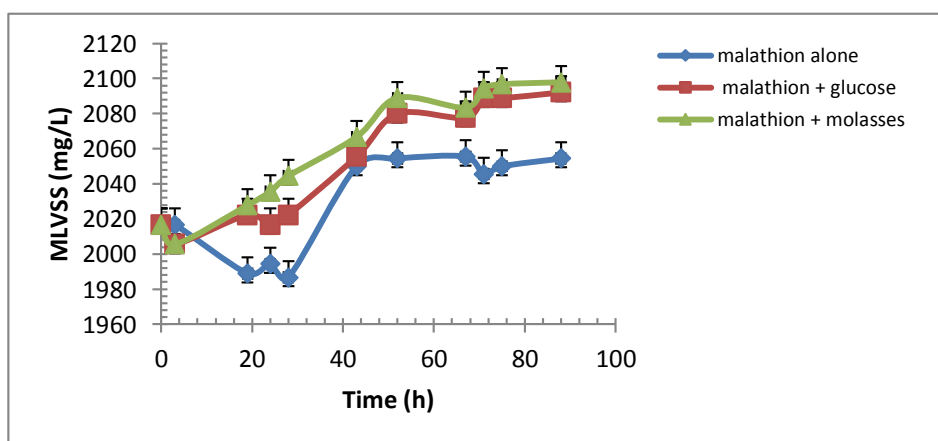


Fig. 4. Time profiles of biomass in batch cultures of activated sludge with and without glucose and molasses (5000 mg/L). Initial malathion and MLVSS concentrations were 60 mg/L and 2000 mg/L, respectively

However, the increased degradation of malathion in the presence of glucose as compared to control experiment was not significant ($p > 0.05$). One cause may be that the additional glucose or molasses supplied easily usable carbon source for cell growth and then prompted malathion transformation. In addition, the degradation of malathion was more efficient on molasses supplemented medium than that on glucose ($p < 0.05$). This is probably due to the fact that, in addition to glucose, molasses contains fructose, raffinose and numerous non-sugar organic materials which could enhance both cell growth and the degradation of malathion. The possible other reason is that the B-vitamin content of molasses (Biotin and Thiamin) could also widely increase cell growth and malathion degradation rate.

However, in the presence of glucose or molasses, the specific consumption rate of malathion was approximately the same compared to the consumption rate without co-substrate addition. On the other hand, it was observed that the lag phase (28h and 45h) in the presence of molasses and glucose, respectively, disappeared when malathion was used alone. But, neither glucose nor molasses were permitted to achieve complete removal of malathion.

Similar results were obtained by Barik et al. (1984), who pointed out that several bacterial strains isolated from sludge sample utilized malathion as their sole carbon source. Furthermore, the addition of glucose to the malathion mixed culture increased the rate of pesticide degradation. More recently, Abraham and Srujana (2014) reported that microbial strains (bacterial and fungal strains) isolated from agricultural fields were able to degrade malathion tested as the sole carbon source.

In contrast, our findings were not agreed with the observations of Singh and Seth (1989), who investigated the biodegradation of malathion by *Pseudomonas sp. M-3* strain and found that no degradation of malathion was observed in the absence of ethanol used as cosubstrate under aerobic condition. Similarly, Xie et al. (2009) observed that malathion could be degraded by *Acinetobacter johnsonii* MA19 strain only in the presence of additional carbon sources (sodium acetate, sodium succinate, glucose and fructose).

This may be related to the type of bacterial culture under consideration and to the conditions under which the culture has been conducted. Thus, in the case of activated sludge culture, the different metabolic strategies associated with various bacterial species, may impact the substrate degradation.

3.5. Analysis and identification of malathion degradation products

At the end of culture (3 days) improved in the presence of malathion tested at 60 mg/L as the sole carbon source, the analysis of the formation of malathion derived degradation products was performed using GC/MS. A typical chromatogram obtained is reported in Fig. 5a. Among all possible metabolites of malathion listed in table 3, only one of them was identified (peak 15.83 min). The mass spectrum of this metabolite showed m/z 302 for the molecular formula $C_8H_{15}O_6PS_2$ with fragment ion peaks at m/z 113, 125, 143 and 211. It was identified as malathion monocarboxylic acid (Fig. 5b). Upon the GC/MS analysis, any noticeable amount of residual malathion was never detected and the conversion to the more toxic analog, malaoxon, did not occur.

Table 3. Structural formulae of malathion metabolites (Bourquin, 1975)

Name	Chemical structure	Name	Chemical structure
Malaoxon		Dimethyl phosphorodithioate, potassium salt	
Malathion monocarboxylic acid		Dimethyl phosphorothioate, potassium salt	
Malathion dicarboxylic acid		Diethyl-maleate	
O-desmrthylmalathion, potassium salt		Mercaptosuccinate	
		Diethyl-succinate	

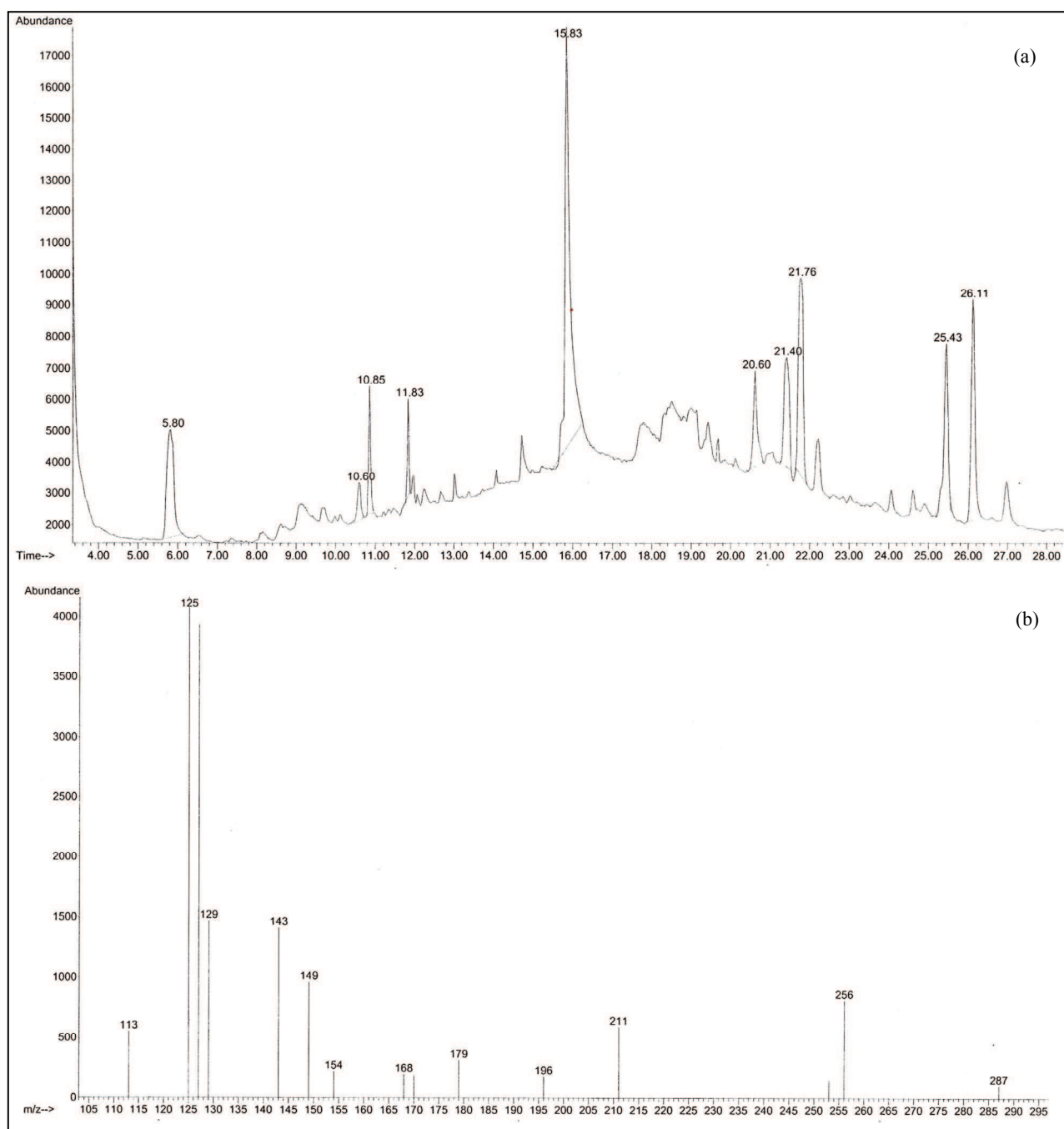


Fig. 5. GC-MS Chromatogram in SIM mode (a) Total ion chromatogram for qualitative analysis of extracted malathion metabolites (b) Mass spectrum of Metabolite X (For experimental conditions see text)

Malathion can be identified using GC (Ait Addi et al., 2014) or GC-MS (Bavcon Kralj et al., 2007; Xie et al., 2013; Zhang et al., 2010) methods. There have been many reports of microorganisms metabolizing malathion to various metabolites (Matsumura and Boush, 1966; Kamal et al., 2008; Singh and Seth, 1989). Carboxylesterase activity, which degrades malathion to its monoacid and diacid, is the predominant degradative pathway. Oxidative desulfuration and demethylation seem to be rather minor metabolic pathways (Matsumura and Boush, 1966). The fact that the carboxylic acid derivative of malathion (malathion monoacid) constitutes the major portion of malathion

metabolites suggests that microorganisms tested are very active in degrading malathion through carboxylesteratic hydrolysis. This is consistent with the observations of Goda et al. (2010), which indicate that various microorganisms (*Pseudomonas sp.*, *Micrococcus lylae* and *Acetobacter liquefaciens*) isolated from soils in Egypt are very active in degrading malathion through carboxylesteratic hydrolysis process.

4. Conclusions

This study showed the potential for using local activated sludge for malathion biodegradation.

Malathion concentrations of 120 mg/L and 140 mg/L inhibited its own degradation as specific pesticide consumption rate was decreased. Such result should be integrated in the wastewater treatment plants operating conditions.

The results showed that molasses was more suitable than glucose as the carbon source for degradation of malathion. Ninety-two per cent (92%) of an initial amount of malathion (60 mg/L) could be degraded in 75 h in the presence of 5000 mg/L molasses. Molasses can be a cost-effective co-substrate of malathion elimination.

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SHORT-TERM RESPONSES OF NITROUS OXIDE FLUXES TO NITROGEN AND PHOSPHORUS ADDITION IN A PEATLAND ON THE TIBETAN PLATEAU

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Abstract

The effects of nitrogen (N) and phosphorus (P) addition to peatland ecosystem on emissions of nitrous oxide (N₂O) were measured using the closed chamber method during one growing season within a peatland on the Tibetan Plateau. The highest N₂O fluxes occurred during late spring (May), while fluxes of N₂O were lowest during early autumn (September). No significant correlations were found between N₂O emissions and soil temperature. Because of the sites stable hydrological conditions no evidence of correlations between N₂O emissions and water content was found. There was a negative correlation between N₂O fluxes and vegetation height. It was clearly shown that the emissions of N₂O were significantly affected by increasing N availability. In contrast to that, no significant effect of P addition on the emissions of N₂O was found in the present study.

Key words: atmospheric deposition, greenhouse gases, high altitude peatland, Tibetan Plateau

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1. Introduction

Peatlands naturally contain large amounts of organic nitrogen (N) within their soils and vegetation, and thus have a significant potential to influence the global atmospheric budget of the greenhouse gas nitrous oxide (N₂O) (Martikainen et al., 1993). The N₂O in soil is biologically produced mainly by the microbiological processes of nitrification and denitrification (Davidson, 1992). These processes depend, to a large extent, on the availability of soil nutrients, which is closely associated with nutrient loading from atmospheric deposition and anthropogenic activities (Granberger et al., 2001). Today all ecosystems are experiencing

increased nutrient (especially nitrogen (N) and phosphorus (P)) loading due to atmospheric deposition and other anthropogenic activities and the increasing trend is considered to be enhanced in the next few decades (Keller et al., 2006). The increasing deposition rates of N and P are thus likely to have affected N₂O fluxes of peatlands, indirectly (e.g. through N deposition on primary production) and directly (e.g. through increasing N availability to microorganisms) (Granberger et al., 2001). Therefore, more researches are needed to quantify the effects of N and P inputting on N₂O emission in the peatland.

Several studies about N₂O fluxes from wetlands focused on soil temperature and hydrology (Chen et al., 2011; Danevčič et al., 2010; Dinsmore

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et al., 2009; Hernandez and Mitsch, 2006). Studies about the effects of N and P availability onto greenhouse gas emissions of peatlands are rare and mostly limited to low elevation peatlands of the boreal zone (Liu and Song, 2010; Nykänen et al., 2002; Zhang et al., 2007). These studies show that N addition generally stimulates N_2O emissions (Granberg et al., 2001; Nykänen et al., 2002). There are uncertain conclusions about the effect of increasing P availability onto N_2O emissions of peatlands. For example, Liu and Song (2010) reported that P addition had limited or no effect on N_2O emissions from peatland soils in Sanjiang Plain (China).

In contrast to that, White and Reddy (2003) show that P application increased the rates of nitrification and denitrification within wetland soils of the Everglades (USA). Until now the effects of the input of N and P of high altitude peatlands have received less attention and no information is available about the impact of N or P on N_2O emissions within those ecosystems. Therefore, the present study investigates the dynamics of N_2O emissions following N and P application during one growing season within a high altitude peatland on the eastern Tibetan Plateau, an area where contains the world's largest extent of high altitude peatlands (Schumann et al., 2008). Next to the availability of N and P this study investigates soil temperature, soil water content and vegetation growth as possible factors to influence the emissions of N_2O .

2. Materials and methods

Our study was conducted in Hongyuan County (33°54'N, 102°36'E), located on the eastern Tibetan Plateau at an altitude of 3500 m a.s.l. The area is characterized by a harsh continental climate. According to recent twenty-year meteorological observations, the mean annual temperature is 1.1 °C. The highest monthly mean temperature is 10.9 °C in July and the lowest is -10.3 °C in January. The annual average precipitation averages is 753 mm, with about 86 % received from May until September.

Sloping percolation mires as well as sloping surface flow mires are the prevalent type of peatlands within the study area (Joosten and Schumann, 2007). Situated within a non sloping (horizontal) peatland, our study site represents flood peatlands that are a further common peatland type within the study area. Flood peatlands are usually situated within river basins and periodically flooded by rivers (Parish et al., 2008). The soil of the study site was classified as peat (Parish et al., 2008). The peat layer of the investigated site is at least 60 cm deep. The vegetation of the study site is dominated by *Carex muliensis*, accompanied by *Caltha scaposa*, *Chamaesium paradoxum*, and *Sanguisorba filiformis*.

To characterize soil chemical properties of the study site, the content of soil organic carbon, organic nitrogen content, total phosphorus content and the pH value were determined from twelve soil cores that

were collected from a depth of 0-10 cm on four randomly selected sampling plots (three soil cores from one plot were mixed as a compound soil sample). Soil chemical properties were determined for all soil samples according to the method described by Liu (1996), i.e. soil organic carbon was determined using Walkley-Black method. Total nitrogen was determined using Kjeldahl method. Total phosphorus was determined by a spectrophotometer after NaOH digestion and soil pH was determined in distilled water at a 1:1 soil:water ratio (weight/volume) with a glass electrode. At the same day as the mentioned soil sampling additional soil cores were taken at every plot to determine soil bulk densities to get an idea about physical soil characteristics of the site.

Within this study three treatments, the separate addition of N, P and the combined addition of N and P, were tested and compared to control plots without treatment. The test included four replicates. In total sixteen plots (2 m × 2 m) were randomly selected and permanently marked in mid May of 2009. The distance between the plots was more than 1 m. to guarantee similar site conditions but to prevent interactions between the plots. N was applied once as NH_4NO_3 at 10 g $\text{N m}^{-2} \text{y}^{-1}$ (100 kg $\text{N ha}^{-1} \text{y}^{-1}$). The supplement of P was carried out once as NaH_2PO_4 at 5 g $\text{P m}^{-2} \text{y}^{-1}$ (50 kg $\text{P ha}^{-1} \text{y}^{-1}$). These rates were 2-3 times higher than the annual N and P requirement of vascular plants on the Tibetan Plateau (Zhou, 2001).

Both substances were dissolved in 2 L of water and evenly distributed within the plots by using a watering can. The control plots were watered with the same amount of pure water. All of the treatment was conducted at the same day in mid May of 2009 and 2010.

The emissions of N_2O were measured within a mixed closed chamber according to Chen et al. (2011). The chamber was made of cylindrical polyvinyl chloride (PVC) and consisted of two parts, a stationary cylinder (without a top and bottom, 30 cm in diameter and 20 cm in height) and a removable covering cylinder (without bottom, 30 cm in diameter and 40 cm in height). The stationary cylinder was plunged 10 cm into the peat and left there throughout the experiment. The cover was placed on top for sampling and sealed air tight by a rubber belt. During the measurements the chamber was covered by aluminum foil to prevent overheating.

All air samples were collected during the morning hours between 09:00 and 11:00 o'clock at six sampling dates (May 20, Jun 20, Jul 20, Aug 24, Sep 24, and Oct 22 in 2010). Before sampling the chambers were closed for 30 min to establish an equilibrium state. At 0, 10, 20 and 40 min intervals, 10 ml headspace samples were extracted into a crimped pre-evacuated glass vial (approximately 10ml with butyl rubber stopper). The concentrations of N_2O within the samples were determined using a gas chromatograph (Hewlett Packard 5890N). The chromatograph was equipped with an electron

capture detector. The N_2O flux rate was calculated by the following formula (Eq. 1):

$$J = \frac{dc}{dt} \cdot \frac{M}{V_0} \cdot \frac{P}{P_0} \cdot \frac{T_0}{T} \cdot H \quad (1)$$

where: J is the flux; dc/dt is the rate of concentration change; M is the molar mass of N_2O ; P is the atmosphere pressure of the sampling site; T is the absolute temperature during the time of sampling; V_0 , P_0 , and T_0 are the molar volume, atmosphere pressure, and absolute temperature, respectively, under the standard condition; and H is the chamber height over the water surface.

We accepted the flux data when there was a good linear regression between the flux and time ($R^2 \geq 0.95$).

The vegetation height of each plot was measured by a rule at air sampling dates. Soil temperature was measured by a soil thermometer at 10 cm depth below soil surface at air sampling dates. Within the study site the mean water table was permanently about 20 cm below soil surface. The soil moisture was determined using a time domain reflectometer (Spectrum Technologies Inc). It was later converted to water-filled pore space (WFPS) (Eq. 2):

$$\text{WFPS} = \frac{\text{VSM}}{(1 - (\text{BD}/\text{PD})) \times 100} \quad (2)$$

where VSM is the volumetric soil moisture, BD is the bulk density, and PD is the particle density.

Statistical analyses were carried out with SPSS statistical package 16.0 (SPSS, Inc., Chicago). Soil temperature, WFPS, plant height, and N_2O fluxes from each sampling date were analyzed with

the two-way ANOVA method to examine the effects of N and P application.

The least significant difference (LSD) at 5% probability level was used to compare the significantly different treatment mean. To explore the effect of time and the changes of treatment effect with time, the two-way ANOVA with repeated measures was also applied with time as the repeated factor. Where necessary, data were normalized by either logarithmic or square-root transformation. Correlations between gas concentrations and environmental parameters were tested using the Pearson correlation coefficient. Significance was accepted at the $P < 0.05$ level of probability.

3. Results

3.1. Site characteristics

The content of organic carbon within the soil of the site was about 140 g kg^{-1} (Table 1), which is typical for river flooded peatlands that are fed by water that is rich of mineral substances according to definition by Succow and Joosten (2001).

The peats C/N ratio of 12.9 and its pH-value of 5.3 (see Table 1) indicate eutrophic and slightly acidic site conditions, which are typical for this kind of peatlands (Parish et al., 2008).

3.2. Soil and plant variables

During the study period soil temperatures varied equally in all plots, with highest values of about 20°C in August and lowest values of about 10°C in October (see Fig. 1a). The soil WFPS was similar in all plots and always above 80 % (see Fig. 1b). Its maximum was reached in August.

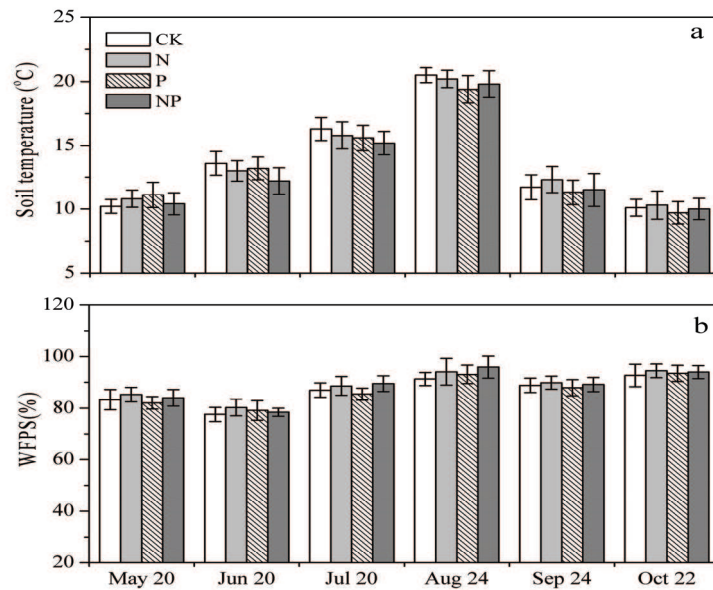
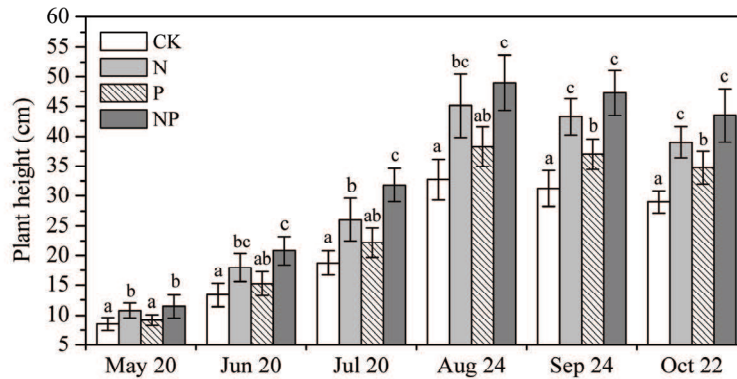


Fig. 1. Soil temperature (a) and WFPS (water-filled pore space) (b) at 10 cm soil depth at different sampling dates. Error bars indicate standard errors ($n=4$). There were no significant differences in soil temperature and WFPS between the different treatments. The treatments were control (CK, 0 kg N , $0 \text{ kg P ha}^{-1} \text{ y}^{-1}$), nitrogen (N, $100 \text{ kg N ha}^{-1} \text{ y}^{-1}$), phosphorus (P, $50 \text{ kg P ha}^{-1} \text{ y}^{-1}$), and nitrogen with phosphorus (NP, 100 kg N , $50 \text{ kg P ha}^{-1} \text{ y}^{-1}$).

Table 1. Peat characteristics of the study site (Means±S.D., n=4)

Organic carbon (g kg ⁻¹)	Total nitrogen (g kg ⁻¹)	C/N	Total phosphorus (g kg ⁻¹)	Bulk density (g cm ⁻³)	pH
138.0±4.2	10.7±0.5	12.9±0.3	1.5±0.1	0.54±0.04	5.3±0.1

**Fig. 2.** Vegetation height at different sampling dates. Error bars indicate standard errors (n=4)

Different lowercase letters indicate significant differences at $P < 0.05$ between treatments with sampling date.

The treatments are control (CK, 0 kg N, 0 kg P ha⁻¹ y⁻¹), nitrogen (N, 100 kg N ha⁻¹ y⁻¹), phosphorus (P, 50 kg P ha⁻¹ y⁻¹), and nitrogen with phosphorus (NP, 100 kg N, 50 kg P ha⁻¹ y⁻¹)

Vegetation height increased rapidly from May and reached its maximum in August. It then declined slightly until the end of the study period (Fig. 2). Vegetation height was significantly higher in treatment plots than in control plots without any treatment. N fertilized plots showed higher vegetation than the ones that were P fertilized. The highest vegetation was observed within sites that were fertilized by the combination of N and P (see Fig. 2).

3.3. N₂O fluxes

The emissions of N₂O showed significant variations during the study period. N₂O emissions tended to decrease between May and July and then markedly increased in August for all treatments (Fig. 3). There was a negative correlation between N₂O fluxes and vegetation height (Table 2). N₂O emissions were significantly affected by N application (Table 3). The mean N₂O emission during the investigation period was 2.9 times higher in N fertilized plots than in control plots without any treatment (see Fig. 3). There was no interaction effect between N and P fertilization on N₂O emissions (Table 3).

Table 2. Pearson correlation coefficients of N₂O fluxes with soil and vegetation variables

Treatments	Soil temperature	WFPS	Vegetation Height
CK	-0.350	-0.115	-0.521**
N	-0.020	-0.329	-0.553**
P	0.004	-0.247	-0.600**
NP	-0.123	-0.371	-0.519**

WFPS is water-filled pore space. **indicate significant correlation at $P < 0.01$, n=24

Table 3. Repeated-measures ANOVA of N₂O fluxes as affected by N and P fertilization during the growing season

Variation source	df	F	p-values
N	1	21.21	0.001
P	1	1.407	0.258
N × P	1	0.649	0.436
Date	5	47.62	<0.001
Date × N	5	8.123	<0.001
Date × P	5	0.378	0.862
Date × N × P	5	0.445	0.815

4. Discussion

Our study revealed N₂O emissions between 0.07 and 1.02 mg m⁻² h⁻², which are comparable to the results of Chen et al. (2011). They are intermediate products of microbial nitrification and denitrification (Bremner, 1997), which depend on soil temperature, soil moisture and soil management (Skiba and Smith, 2000). Previous studies indicated that denitrification rates increased rapidly when WFPS exceeded 70 %, whereas nitrification was the dominant source of N₂O in the range of 30-70 % of WFPS (Davidson, 1992). During our study, the water level of all plots was permanently about 20 cm below soil surface and WFPS was always above 80 % in all plots (Fig 1b), suggesting that denitrification was the dominant source of N₂O. The highest N₂O emissions were observed in May.

This result is similar to observations of Danevčič et al. (2010), who found the highest N₂O emissions in peatlands of Southern Europe in late spring. This could be attributed to an increasing availability of organic C and N for denitrification after the thawing of the frozen soil (Møkved et al., 2006; Teepe et al., 2001).

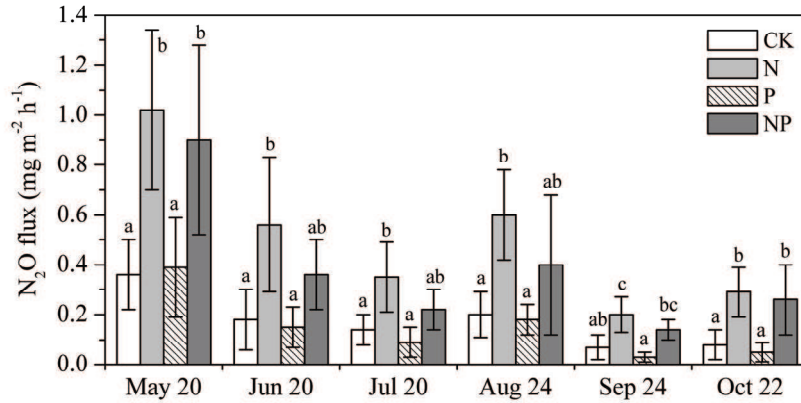


Fig. 3. N₂O emissions as affected by N and P fertilization at different sampling dates. Error bars indicate standard errors (n=4). Different lowercase letters indicate significant differences at $P < 0.05$ between treatments with sampling date. The treatments are control (CK, 0 kg N, 0 kg P ha⁻¹ y⁻¹), nitrogen (N, 100 kg N ha⁻¹ y⁻¹), phosphorus (P, 50 kg P ha⁻¹ y⁻¹), and nitrogen with phosphorus (NP, 100 kg N, 50 kg P ha⁻¹ y⁻¹)

The observed decline of N₂O fluxes from May until July was probably caused by high rates of NO₃-N uptake by rapidly developing vegetation (Gao et al., 2008). In addition to that, increased oxygen consumption by plant root respiration during the growing season may also result in the increase of denitrification, which may stimulate soil N₂O production (Klemetsson et al., 1987; Manea et al., 2013). In late August, when plants went into a desiccating period and their production ceased, NO₃-N again accumulated within the soil. The concentration of soil oxygen may increase when plants stop growing this can limit the denitrification of soil. This assumption was approved by the results of our correlation analysis between vegetation height and N₂O emissions (Table 2). Vegetation height can be used as indicator for vegetation biomass (Ding et al., 2005). During the same time the soil temperature, that stimulates soil microbial activity (Skiba and Smith, 2000), reached its highest values and may be a further explanation for increasing N₂O emissions in August.

With decreasing soil temperatures, and with that due to a reduced soil microbial activity, the emissions of N₂O were reduced in September and October. N₂O emissions were higher during spring than in summer and autumn, but there was no correlation between N₂O fluxes and the investigated soil variables (see Table 3), which may be caused by the change of soil temperature and WFPS only in a narrow range and by seasonal effect of vegetation on substrate content in soil. Similar results were found within alpine grasslands of the Tibetan Plateau by Pei et al. (2003) and Jiang et al. (2010). It is obvious that N₂O emissions of peatlands are affected by a combination of different factors that require further research.

Our study shows that N application stimulates N₂O emissions. Similar results were presented by Augustin et al. (1998) for peatlands in northeastern Germany and by Maljanen et al. (2003) for boreal

forested peatlands in Finland. The availability of N is regarded as the most important factor of N₂O emissions of soils (Hou et al., 2000; Trujillo-Tapia et al., 2008), as it is the substrate of nitrification and denitrification. There was an interaction between N and sampling date to N₂O emission (Table 3), that stand for the response extent of N₂O to addition of N varied seasonally. For example, N₂O fluxes were 3.6 times higher in N fertilized plot than that in the control plot in October, but it was only 2.5 times higher in July. This variety can be attributed to the seasonal variety of plant growth, soil temperature and moisture.

The application of P did not show significant effects on the emission of N₂O in the present study, which is consistent with previous studies in peatlands of the Sanjiang Plain that were presented by Liu and Song (2010). Similar results were shown by Steudler et al. (2002) in tropical forests and pastures and by Zhang and Han (2008) in grasslands in northern China. In contrast to that, several studies report about enhanced N₂O emissions in response to P addition in tropical forests (Keller et al., 1988) and in abandoned croplands of northern China (Zhang and Han, 2008). However, the mechanisms of increased N₂O emissions in response to P are still not clear and require further investigation. P addition also had little effect on N₂O emissions' response to N addition, as measured by the N and P interaction in the ANOVA models (Table 3). This indicates that the amount of N₂O emissions as a reaction to the addition of N or P did not depend on the addition of the other nutrient in this peatland.

As discussed above, N₂O emissions were significantly affected by N fertilization. The mean N₂O emissions during the study period were about 3 times greater in fertilized plots than in unfertilized control plots. The results of this study highlight the importance of N input from atmospheric deposition or fertilization in controlling N₂O emissions from high altitude peatlands. Our study area, located on

the eastern Tibetan Plateau, contains the world's largest extent of high altitude peatlands (Schumann et al., 2008) and thus plays an important role in the N_2O budget of peatlands in the world. Therefore, our study has important implications for predictions about future contributions of high altitude peatlands of the Tibetan Plateau, and possibly other alpine regions of the world, to the global N_2O budget under future changes in the deposition rates of atmospheric N deposition or N fertilization application.

5. Conclusions

The emissions of N_2O from high altitude peatlands affected by N and P addition were measured during the growing season within a high altitude peatland of the Tibetan Plateau. The results show that there is no correlation between N_2O fluxes and soil temperature and water content.

Lack of the correlation between N_2O flux and soil variables may be caused by the relatively stable site conditions with only minor changes of soil temperature and WFPS and by seasonal effect of vegetation on substrate content in soil. Increasing N availability led to increasing N_2O emissions. The addition of P had no significant effect on N_2O fluxes. The results demonstrate that, in a short term, increasing N availability may play a major role in controlling the fluxes of N_2O of alpine peatlands, but that the increased P availability on N_2O emissions was negligible.

More research is needed to assess long-term effects of increasing availabilities of N and P on N_2O fluxes in high altitude peatlands.

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ADSORPTION PROPERTIES OF ACTIVATED CARBON FROM WILD PLANT PREPARED BY CHEMICAL ACTIVATION

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Abstract

Activated carbon was prepared from renewable plant material, that is *Euphorbia rigida*, by chemical activation using zinc chloride as activating reagents. The adsorption of Basic Blue 9 (BB9) onto activated carbon was investigated in a batch system with respect to contact time, pH and temperature from aqueous solutions. The experimental data indicated that the adsorption isotherms are well described by the Langmuir isotherm model and the calculated maximum adsorption capacity of activated carbon was 155.62 mg g⁻¹ at 40°C. The experimental data fitted very well to pseudo-second order kinetic model and also followed by the intraparticle diffusion model up to 60 min. The thermodynamic parameters such as change of free energy, enthalpy and entropy of adsorption were also calculated to estimate the nature of adsorption. The results show that activated carbon prepared from *Euphorbia rigida*, which is a wild and abundant plant, by zinc chloride chemical activation could be employed as low-cost material to compare with commercial activated carbon for the removal textile dyes from textile wastewater processes.

Key words: activated carbon, adsorption, basic dye, isotherms, kinetics

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1. Introduction

Effluents from textile dyeing and finishing processes are usually highly colored with a large amount of suspended organic solids, which are important sources of water pollution due to the fact that these effluents destroy aquatic life and are also poorly biodegradable or resistant to environmental conditions (Namane et al., 2005; Tsai et al., 2001). In this manner, these kinds of pollutants treat prior to their discharge into the receiving water bodies. Many of physical, chemical and biological methods have been used for the treatment of dye-containing wastewater (Özcan and Özcan, 2004). One of the effective methods, which is the adsorption technique, can be used for the removal of textile effluents from wastewater (Ho and McKay, 1998; Luis et al., 2014; Sun et al., 2014; Won et al., 2006; Wu et al., 2005a).

Activated carbons are the most promising used adsorbents in the adsorption process because of their excellent adsorption capacity for textile dye

effluents. Although commercially activated carbons have high surface area and high adsorption capacity, they are expensive and have relatively high operation costs. In this respect, these have led many researchers to use low-cost plant and wood based materials, which are contain a high carbon content and low ash content, as precursors for activated carbon production for the removal of textile dye effluents by adsorption. Numerous low-cost plants, agricultural and/or wood based materials such as coconut tree sawdust, silk cotton hull, sago industry waste, banana pith, maize cob (Kadirvelu et al., 2003), jute fiber (Senthilkumaar et al., 2005), pistachio shells (Attia et al., 2003; Wu et al., 2005b), palm kernel shell (Jumasiah et al., 2005), date piths (Banat et al., 2003a, b), coir pith (Kavitha and Namasivayam, 2007), rice husk (Guo et al., 2003; Mohamed, 2004; Rahman et al., 2005), guava seeds (Rahman and Saad, 2003), mango seed kernel powder (Kumar and Kumaran, 2005), rubberwood sawdust (Prakash Kumar et al., 2005), bagasse fly ash (Gupta et al.,

2000), raw bagasse (Valix et al., 2004), mahogany sawdust (Malik, 2003), pine wood (Tseng et al., 2003), rosewood sawdust (Garg et al., 2004), corncob wastes (Wu et al., 2001), bamboo dust (Kannan and Meenakshisundaram, 2002), sugarcane bagasse (Kaushik et al., 2009), olive waste cake (Baccar et al., 2010) and have been used for the production of activated carbon for the removal of the textile dye effluents.

More recently, some authors started to look at the surface chemistry of activated carbons in order to interpret some results of dye adsorption experiments (Faria et al., 2004; Pereira et al., 2003; Rodriguez et al., 2009).

One of the renewable plant materials, which is *Euphorbia rigida*, has received as an activated carbon source in this study due to a lack of information on its adsorption abilities. *E. rigida* is a member of the Euphorbiaceae family plant and it grows mostly in arid land regions in Anatolia, Turkey. This family of plants included around 2000 species, ranging from small herbs to large trees. They can produce milky latex, which yields wide range of chemical such as rubber, oils, terpenes, waxes, hydrocarbons, starch, resins, tannins, and balsams of interest to various industries but it does not use for the food production (Calvin, 1978; Nemethy et al., 1981; Pütün et al., 2001).

The adsorption properties of activated carbons were found to strongly depend on the activation process and the nature of source materials. Activated carbons could be prepared by either gas or chemical activation. Gas activation involves carbonization at 400-500°C to eliminate the bulk of the volatile matter and then partial gasification of the materials at the range of temperature of 800-1000°C under mild oxidizing conditions. Simultaneous carbonization and activation can also be obtained chemically by impregnation with dehydrating agents such as phosphoric acid, potassium sulfide and zinc chloride at temperatures between 500-900°C (Yang, 2003). Chemical activation by ZnCl_2 improves the large carbon surface area (Tsai et al., 2001). In comparison with gas activation, there are two important advantages of chemical activation. One of them is the lower temperature in which the process is achieved. The other is that the global yield of the chemical activation tends to be greater because burn-off char is not required (Osmond, 2000; Rio et al., 2005; Wu et al., 2005b).

In this study, *E. rigida*, which is a plant-based material and a biomass source, has been used for the preparation of activated carbons with zinc chloride chemical activation and its ability to remove Basic Blue 9 (BB9) dye from aqueous solutions. Basic Blue 9 has widely used such as coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stocks, etc. Although BB9 is not strongly hazardous, it can cause some harmful effects. For instance; on inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning

sensation and may cause nausea, vomiting, diarrhea and gastritis. A large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturition, and methemoglobinemia-like syndromes (Bhattacharyya and Sharma, 2005; Kumar and Kumaran, 2005).

The study of adsorption equilibrium isotherms, kinetics and thermodynamic is essential in supplying the basic information required for the design and operation of adsorption equipments for wastewater treatment. The Langmuir, Freundlich and Dubinin Radushkevich (D-R) isotherm models; and the Lagergren first-order, pseudo-second-order kinetic and intraparticle diffusion models have been considered.

2. Experimental

2.1. Preparation of activated carbon and dye solutions

Euphorbia rigida was used in this study as a source of activated carbon, collected from nearby Afyon, Turkey. It was harvested between May and July, and it was then dried at room temperature and stored in a cool and dark room for 3 months. Production of activated carbon has involved by the carbonization of *E. rigida* in a negligibly ventilated atmosphere to drive out volatiles, leaving a porous carbon structure with a high surface area. Zinc chloride as a chemical reagent added during the chemical activation process help produce more effective adsorbent. During the activation procedure, 30 g of *E. rigida* was impregnated with a solution of 25% ZnCl_2 by weight for 24 h and then filtered and the resulting chemical loaded *E. rigida* was placed in a furnace and heated ($10^\circ\text{C min}^{-1}$) to the final carbonization temperature of 500°C for 30 min. The impregnation ratio in the activated carbon preparation was 1:1. In all experiments, heating rate was kept constant. After cooling, the activated carbon was repeatedly washed with deionized water to remove residual chemicals until a negative chloride test was obtained with 0.1 M AgNO_3 and dried at 110°C. The carbonized material was sieved to 125-250 μm size and used for adsorption experiments.

Activated carbon was characterized with respect to the surface area at 77 K by means of a standard BET procedure N_2 adsorption (Quantachrome Inst., Nova 2200e Surface Area Analyzer). BET equation was used to calculate the specific surface area. Before the measurements activated carbon was degassed at 300°C for 3 h. The surface area of activated carbon is 509 $\text{m}^2 \text{g}^{-1}$.

A commercial textile dye Basic Blue 9 (BB9) (methylene blue C.I. 52015) was obtained from Merck, Germany and used without further purification. The chemical structure of BB9 is depicted in Fig. 1. A stock solution of dye (BB9) was prepared by dissolving an accurate quantity of dye in deionized water. Other concentrations prepared from stock solution by dilution varied between 100 and

400 mg dm⁻³ and the pH of the working solutions was adjusted to desired values with 0.1 M HCl or 0.1 M NaOH. Fresh dilutions were used for each experiment.

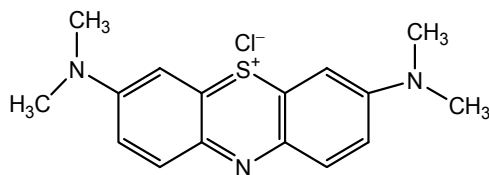


Fig. 1. The chemical structure of BB9

2.2. Adsorption experiments

The pH experiments were carried out by 50 ml of a 200 mg dm⁻³ dye solutions with 0.1 g of activated carbon and the pH was carefully adjusted between 3 and 10 with adding a small amount of dilute HCl or NaOH solution using a pH meter. The dye solutions were stirred using a mechanical magnetic stirrer in a 100-ml erlenmeyer sealed with parafilm to avoid evaporation for 200 minutes at 250 rpm.

The optimum pH was then determined as 6 and used throughout all adsorption experiments, which were conducted at various time intervals and temperatures (20, 30 and 40°C), to determine the adsorption equilibrium time and the maximum removal of basic dye. The solutions were centrifuged and then subjected to quantitative analyses. The equilibrium concentrations of each solution were measured by spectrophotometer (Shimadzu UV-2101PC) at the λ_{max} value, which is 665 nm for BB9. The amount of the dye adsorbed onto activated carbon surface was determined by the difference between the initial and remaining concentration of the dye solution.

The adsorption of BB9 onto activated carbon was also evaluated at constant temperatures of 20, 30 and 40°C for the adsorption isotherms.

3. Results and discussion

3.1. Effect of pH

Fig. 2 indicates the effect of pH on the removal of basic dye (BB9) onto activated carbon from aqueous solution. It was observed that the adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization of adsorbate. At lower pH more protons will be available, thereby decreasing electrostatic attractions between positively charged dye cations and positively charged adsorption sites and therefore ionic repulsion between the positively charged surface and the cationic dye molecules to cause a decrease in dye adsorption. When the pH of the solution is increased, the positive charge on solution interface decreases and the adsorbent surface appears negatively

charged. A higher adsorption capacity was obtained at higher pH values due to the abundance of OH⁻ ions therefore increasing electrostatic attractions between positively charged dye cations and negatively charged adsorption sites. As it can be seen from Fig. 2, the maximum BB9 removal was observed at pH 6-10. Thus pH 6 was selected as the optimum pH value for all further experiments due to the advantage of neutral pH value.

3.2. Effect of contact time and temperature

The effect of contact time on the amount of BB9, adsorbed onto activated carbon at various temperatures (Fig. 3) was also investigated with 250 mg dm⁻³ BB9 solutions. The removal of BB9 onto activated carbon was rapid initially and then slows down gradually until it attained. Maximum adsorption capacity of BB9 onto activated carbon was observed at 150 min, it can be said that beyond which there is almost no further increase in the adsorption and it is thus fixed as the equilibrium contact time.

The equilibrium adsorption capacity of BB9 onto activated carbon was also affected by temperature and increased with increasing temperature from 20 to 40°C which indicates that the adsorption of BB9 onto activated carbon surface was favored at higher temperatures and it is controlled by an endothermic process.

This is partly due to a strong of the attractive forces (Singh, 1998; Tsai et al., 2004) between BB9 and activated carbon.

3.3. Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important data to solve the mechanism of the adsorption systems. In this manner, the Langmuir (1918) (Eq. 1), Freundlich (1906) (Eq. 2) and Dubinin-Radushkevich (D-R) (1947) isotherm equations were used to interpret the experimental data.

The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogenous sites within the adsorbent and has found successful application many adsorption processes of monolayer adsorption. The linear form of the Langmuir isotherm equation (1918) is represented by the following equation:

$$C_e/q_e = 1/q_{\text{max}}K_L + C_e/q_{\text{max}} \quad (1)$$

where q_e is the equilibrium dye concentration on the adsorbent (mg g⁻¹), C_e is the equilibrium dye concentration in the solution (mg dm⁻³), q_{max} is the monolayer adsorption capacity of the adsorbent (mg g⁻¹), and K_L is the Langmuir adsorption constant (dm³ mg⁻¹) and related to the free energy of adsorption. Fig. 4 shows Langmuir plots for the adsorption of BB9 onto activated carbon.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. A linear form of the Freundlich equation (1906) is (Eq. 2):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (2)$$

where: K_F ($\text{mg g}^{-1}(\text{dm}^3 \text{mg}^{-1})^{1/n}$) and n (dimensionless) are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

Freundlich plots for the adsorption of BB9 onto activated carbon at various temperatures is shown in Fig. 5. The (D-R) isotherm is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption of dye. The linear form of (D-R) isotherm equation (1947) is (Eq. 3):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (3)$$

where β is a constant related to the mean free energy of adsorption per mole of the adsorbate ($\text{mol}^2 \text{kJ}^{-2}$), q_m is the theoretical saturation capacity, and ε is the Polanyi potential, which is equal to $RT \ln (1+1/C_e)$, where R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant, and T (K) is the absolute temperature.

Fig. 6 indicates the D-R isotherm for BB9 adsorption onto activated carbon. The Langmuir, Freundlich and D-R parameters for the adsorption of BB9 onto activated carbon are listed in Table 1. It is evident from these data that the surface of activated carbon is made up of homogeneous adsorption patches. In other words, the Langmuir isotherm model fits well when the r^2 values are compared Table 1. The Langmuir model correlation coefficients are a range of 0.989-0.999, the Freundlich model correlation coefficients between 0.878 and 0.895 and the D-R model correlation coefficients are a range of 0.885-0.942.

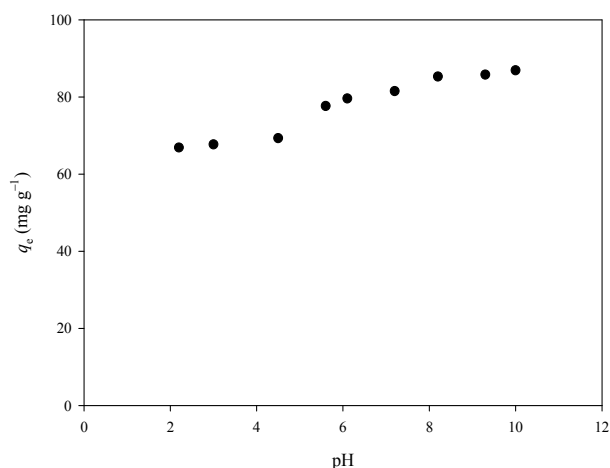


Fig. 2. Effect of pH for the adsorption of BB9 onto activated carbon at 20°C

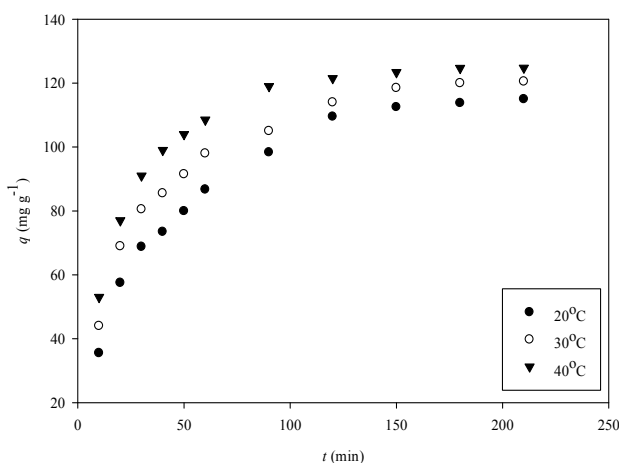


Fig. 3. Effect of contact time for the adsorption of BB9 onto activated carbon from a concentration of 250 mg dm^{-3} and various temperatures

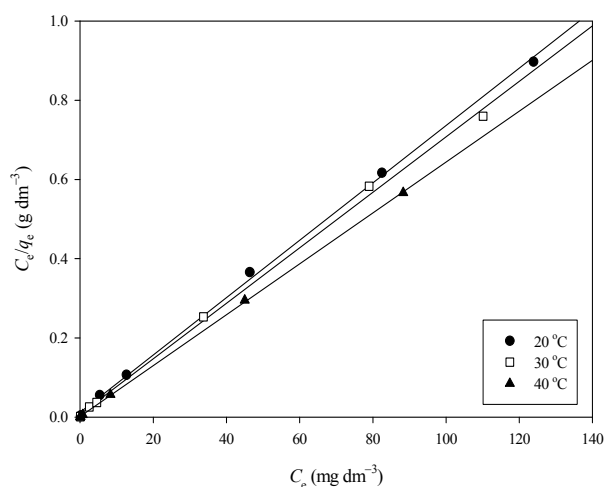


Fig. 4. Langmuir plots for the adsorption of BB9 onto activated carbon at various temperatures

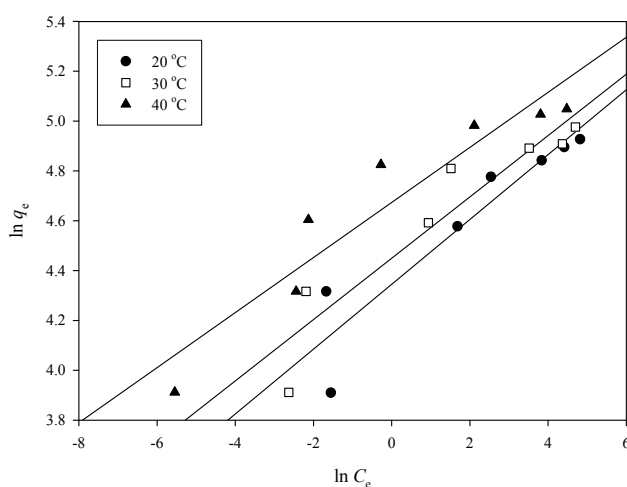


Fig. 5. Freundlich plots for the adsorption of BB9 onto activated carbon at various temperatures

Table 1. Adsorption isotherm constants for the adsorption of BB9 onto activated carbon at various temperatures

	<i>t</i> (°C)		
	20	30	40
Langmuir			
$q_{\max}$ (mg g ⁻¹)	138	142	155
K_L (dm ³ mg ⁻¹)	0.599	0.997	4.108
r_L^2	0.999	0.989	0.999
Freundlich			
n	7.7	8.1	9.1
K_F (mg g ⁻¹ (dm ³ mg ⁻¹) ^{1/n})	77.12	85.62	107.09
r_F^2	0.878	0.886	0.895
Dubinin–Radushkevich (D–R)			
$q_{\max}$ (mg g ⁻¹)	200.32	208.63	226.64
β (mol ² kJ ⁻²)	9.73x10 ⁻⁴	8.39x10 ⁻⁴	6.43x10 ⁻⁴
r_{D-R}^2	0.885	0.914	0.942

The adsorption capacity of activated carbon obtained from Langmuir isotherm equation for BB9 in this study is comparable and was found to be higher than that of many corresponding adsorbents reported in the literature (Table 2).

3.4. Kinetics of adsorption

The kinetics of adsorption is one of the most important characteristics in defining the efficiency of adsorption. Various kinetic models have been proposed by different research groups where the adsorption has been treated as the Lagergren first-order (1898) (Eq. 4), a pseudo-second-order (Ho and McKay, 1998) (Eq. 5), and intraparticle diffusion (Weber and Morris, 1963) (Eq. 6). The Lagergren first-order kinetic model equation (1898) is:

$$\ln(q_e - q_t) = \ln q_e - k_{\text{ads}} t \quad (4)$$

where q_e and q_t are the amounts of the dye adsorbed at equilibrium and at time t , in mg g⁻¹, and k_{ads} is the Lagergren first-order rate constant (min⁻¹), was applied to the adsorption of BB9.

The pseudo-second-order kinetic model (Ho and McKay, 1998) is expressed as:

$$t/q_t = 1/k_2 q_2^2 + (1/q_2)t \quad (5)$$

where q_2 is the maximum adsorption capacity (mg g⁻¹) for the pseudo-second-order adsorption, k_2 is the equilibrium rate constant for the pseudo-second-order adsorption (g mg⁻¹ min⁻¹). The kinetic data for the adsorption of BB9 under various conditions were calculated from the related plots (Fig. 7 and Fig. 8) and were given in Table 3.

As it can be seen, these adsorption systems follow a pseudo-second order kinetic model. When the temperature of the solution is increased the calculated q_e values and rate constants are also increased for the pseudo-second order model. The correlation coefficients calculated for the pseudo-second order model fitting are higher than the ones obtained in the case Lagergren first-order model is used. These results imply that the adsorption system

studied obeys to the pseudo-second order kinetic model.

The Lagergren first-order and pseudo-second-order kinetic models can not identify the diffusion mechanism and the kinetic results were then analyzed by using the intraparticle diffusion model. The intraparticle diffusion equation (Weber and Morris, 1963) can be written by following:

$$q_t = k_p t^{1/2} + C \quad (6)$$

where C is the intercept, and k_p is the intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}).

When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously (Bhattacharyya and Sharma, 2004; Chen et al., 2003; Kannan and Sundaram, 2001). The slope of linear portion from the figure (not shown) can be used to derive values for the rate parameter, k_p , for the intraparticle diffusion, given in Table 3.

The correlation coefficients (r_p^2) for the intraparticle diffusion model are also lower than the pseudo-second order model, whereas this model indicate that the adsorption of BB9 onto activated carbon may be followed by an intraparticle diffusion model up to 60 min.

The pseudo-second order rate constants for BB9 onto activated carbon indicate a steady increase with temperature. The values of rate constant were found to increase more than two times at a concentration of 250 mg dm⁻³ for activated carbon with an increase in the solution temperatures from 20 to 40°C.

3.5. Thermodynamic parameters

Because K_L is equilibrium constant, its dependence with temperature can be used to estimate thermodynamic parameters, such as change in the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process (Eqs. 7-8).

Table 2. Adsorption results of BB9 from the literature by activated carbons obtained from various plants, agricultural and wood based materials and operating conditions

Activated carbon source	Operating conditions				
	pH	t (°C)	Initial concentration range (mg dm ⁻³)	Adsorbent dosage (g dm ⁻³)	Adsorption capacity (mg g ⁻¹)
Fir wood (Wu et al., 2005a)	6.6	30	200	1.00	70.05
Coconut tree sawdust (Kadirvelu et al., 2003)	4.72-5.07	31	25	5.00	4.70
Silk cotton hull (Kadirvelu et al., 2003)	4.72-4.95	31	25	5.00	2.40
Sago waste (Kadirvelu et al., 2003)	4.72-3.62	31	25	5.00	4.51
Maize cob (Kadirvelu et al., 2003)	4.72-4.12	31	25	5.00	5.00
Banana pith (Kadirvelu et al., 2003)	4.72-4.02	31	25	5.00	4.67
Jute fiber (Senthilkumaar et al., 2005)	5-10	28	50-200	0.40-4.00	225.64
Pistachio shell (Attia et al., 2003)	4.2	--	150	1.00	129.00
Pistachio shell KOH impregnated (Wu et al., 2005b)	6.6	30	200	---	320.9
Palm kernel shell (Jumariah et al., 2005)	7.0	28	100-700	1.00	311.72
Date pits (Banat et al., 2003a)	---	25	20-400	5.00	123.1
Coir pith (Kavitha and Namasivayam, 2007)	6.9	35	10-40	2.00	5.87
Mango seed kernel powder (Kumar and Kumaran, 2005)	8.0	30	20-100	6.67	142.86
Rice husk H ₃ PO ₄ impregnated (Singh and Srivastava, 2001)					333.3
Corn cob (El-Hendawy, 2003)	---	25	---	1.00	577.03
<i>Euphorbia rigida</i> ZnCl ₂ impregnated (in this study)	6.0	40	100-400	2.0	155.62

Table 3. Kinetic parameters for the adsorption of BB9 onto activated carbon at various temperatures

	t (°C)		
	20	30	40
Lagergren			
k _{ads} (min ⁻¹)	2.44x10 ⁻²	2.70x10 ⁻²	3.61x10 ⁻²
q _e (mg g ⁻¹)	108	108	122
r ₁	0.989	0.966	0.925
Pseudo-second-order			
k ₂ (g mg ⁻¹ min ⁻¹)	2.63x10 ⁻⁴	3.58x10 ⁻⁴	5.19x10 ⁻⁴
q ₂ (mg g ⁻¹)	132	133	135
r ₂	0.998	0.999	0.999
Intraparticle diffusion			
k _p (mg g min ^{-1/2})	10.6	11.1	11.9
C (mg g ⁻¹)	6.44	14.5	20.6
r _p	0.966	0.952	0.957

$$\Delta G^{\circ} = -RT \ln K_L \quad (7)$$

$$\ln K_L = -\Delta G^{\circ} / RT = -\Delta H^{\circ} / RT + \Delta S^{\circ} / R \quad (8)$$

The plot of $\ln K_L$ as a function of $1/T$ (Fig. 9) yields a straight line from which ΔH° and ΔS° were calculated from the slope and intercept, respectively. The results are given in Table 4. Generally, the change of free energy for physisorption is between -20 and 0 kJ mol⁻¹, the physisorption together with chemisorption is at the range of -20 to -80 kJ mol⁻¹ and chemisorption is a range of -80 to -400 kJ mol⁻¹ (Jaycock and Parfitt, 1981). The overall standard free energy change during the adsorption process was negative for the experimental range of temperatures (Table 4), corresponding to a spontaneous and a boundary of chemical process of BB9 adsorption (Chu et al., 2004). The positive value of the enthalpy change (+73.08 kJmol⁻¹) indicates that the adsorption is the boundary of physisorption together with chemisorption in nature involving strong forces of attraction and is also endothermic (Yu et al., 2001).

Table 4. Thermodynamic parameters calculated from the Langmuir isotherm constant, K_L , for the adsorption of BB9 onto activated carbon

t (°C)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
20	-29.65	73.08	349.13
30	-31.94		
40	-36.68		

The positive entropy change (ΔS°) value (+349.13 J mol⁻¹ K⁻¹) corresponds to an increase in the degree of freedom of the adsorbed species.

4. Conclusions

From the foregoing experiments, the reasonable results were obtained that activated carbon from *E. rigida* by ZnCl₂ activation is an effective adsorbent for removing BB9 from aqueous solution. Therefore this adsorbent can be represented as a suitable adsorbent and environmentally clean utilization of wastewater.

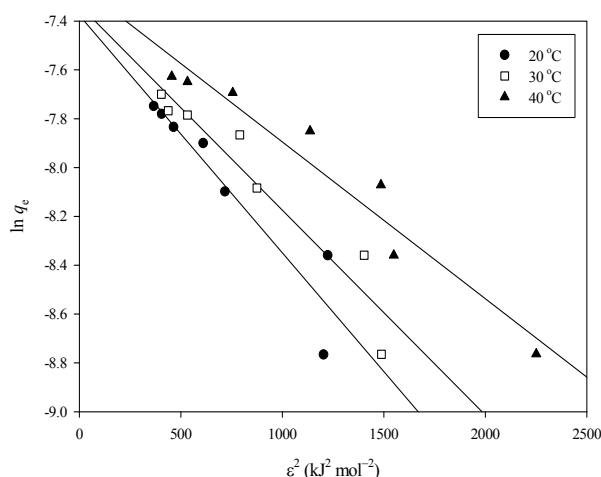


Fig. 6. D-R plots for the adsorption of BB9 onto activated carbon at various temperatures

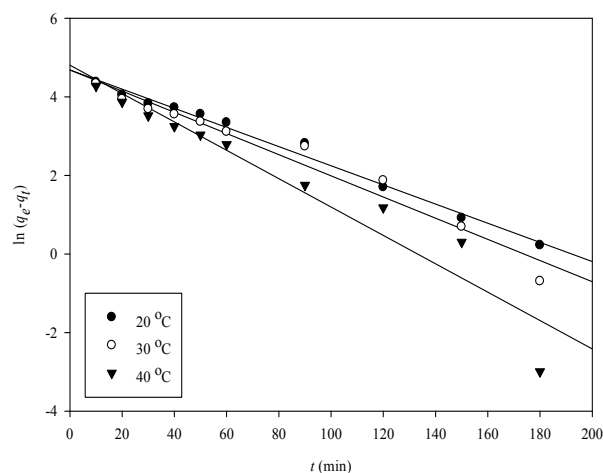


Fig. 7. Lagergren first-order kinetic plots for the adsorption of BB9 onto activated carbon at various temperatures

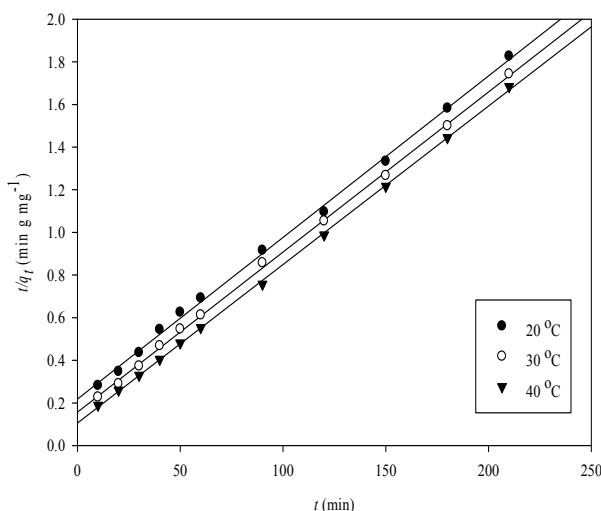


Fig. 8. Pseudo-second-order kinetic plots for the adsorption of BB9 onto activated carbon at various temperatures

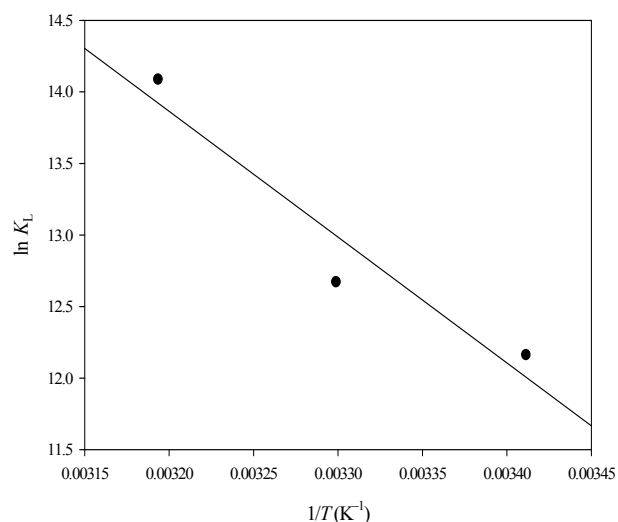


Fig. 9. Plot of $\ln K_L$ versus $1/T$ for estimation of thermodynamic parameters for the adsorption of BB9 onto activated carbon

The adsorption isotherms of BB9 onto activated carbon were analyzed according to Langmuir, Freundlich and D-R models. The Langmuir isotherm model for BB9 adsorption was fitted well with the experimental equilibrium data than the other isotherm models. The mechanism of the dye-activated carbon interaction is thus likely to be very complicated involving a wide range of sites differing in a number of aspects including energy considerations.

The kinetics of adsorption of BB9 onto activated carbon is studied on the basis of the Lagergren first-order, pseudo-second-order kinetic and intraparticle diffusion models under various contact time and temperatures. The high adsorption capacity of activated carbon in basic solutions (pH after 6.0) is due to the strong electrostatic interactions between its adsorption site and dye cation.

The enthalpy change (ΔH°) for the adsorption process was indicative of the endothermic nature of adsorption and a boundary of chemical adsorption. The ΔG° values were negative therefore the adsorption was spontaneous and the positive value of ΔS° suggests an increased randomness at the solid/solution interface and no significant changes occur in the internal structure of the adsorbent through the adsorption of BB9 onto activated carbon.

Acknowledgements

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CAUSAL ANALYSIS ON THE SPECIFIED PAROXYSMAL WATER POLLUTION INCIDENTS IN THE HUAI RIVER BASIN, CHINA

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Abstract

In the Huai River Basin, pollutant masses are frequently concentrated into dams and sluices, which are subsequently discharged and destroying the downstream ecology and environment. This phenomenon has been termed the specified paroxysmal water pollution incident (SPWPI), which has attracted worldwide attention as a large-scale water pollution problem. Studies of the formation mechanism of SPWPIs have become an urgent topic for fundamental research in water pollution prevention and control. In this paper, five serious SPWPIs (in 1989, 1994, 1995, 2000 and 2004) are selected to investigate the variation of meteorology, hydrology, water quality, pollution source (ammonium and chemical oxygen demand) and operation of dams and sluices during the period of events occurring in the middle and lower regions of Shaying River. The results show that the specific water pollution incident always occurred during the first flood period before the flood season (June-September). The elevated emissions of pollutants, increased dam construction and irrational regulations cause the accumulation of pollutants upstream of the dam, and directly induce the incidents. Moreover, the first heavy precipitation before the flood season is an important factor, which will directly trigger the flood discharge from dams and sluices with high concentrations of pollutants from upstream to downstream. The pollution will be further aggravated if no rain falls in the main stream of Huai River and southern mountainous region at the same time. This research is expected to identify the causes of the deterioration of water environments and provide scientific and technological support to prevent the paroxysmal water pollution incidents. It is also intended to guide the implementation of water pollution controls and ecological restoration in the Huai River Basin.

Key words: Causal analysis, Huai River Basin, operation of dams or sluices, specified paroxysmal water pollution incident (SPWPI)

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1. Introduction

Huai River Basin is a highly populated region with one of the highest densities of water projects. It also experiences prominent water pollution problems in the seven large river basins of China (Zhang et al., 2010). In order to control floods and relieve droughts in this basin, more than 11,000 dams and sluices have been constructed, and a complete water project system has been established (Ning, 2001). Currently, over 83% of rivers in Huai River Basin have been

polluted with the main pollutants comprising of ammonium (NH₃-N) and chemical oxygen demand (COD), due to the excessive discharge of industrial and sewage pollution (Zhang et al., 2011). In the pre-flood season, the upstream dams and sluices are left open as to discharge stored water for flood control. Thus, the accumulated pollutant masses in the upstream of the dams and sluices are discharged at the same time as runoff.

The downstream aquatic ecology and environment is then destroyed by the highly polluted

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runoff. In this study, these incidents are termed paroxysmal water pollution incidents (SPWPI) in the Huai River Basin (Chen et al., 2005; Shen and Yang 2001; Zhang et al., 2010). Over the past several decades, SPWPI has frequently occurred and water pollution has become a new serious disaster affecting the Huai River Basin along with the rapid regional development and excessive emissions of pollutants.

Since the first SPWPI occurred in 1989, nearly 200 SPWPIs have occurred (Shen and Yang, 2001), and the most harmful incidents were in 1994 and 2004, which even shocked the world. Particularly, in July 1994, over 200 million m³ of polluted water was centralized released from the upstream of dams and sluices due to a sudden heavy storm in the upper Shaying River in the Basin. The polluted water instantly killed fish and shrimps along the mainstream, and forced the waterworks to shut down for nearly two months. The drinking water for millions of people ran out and the total economic losses reached hundreds of millions dollars.

SPWPIs in the Huai River Basin have been concerned seriously all over the world. Since 1994, billions of dollars have been spent by the Chinese government on pollution control. Moreover, large numbers of statutes and regulations have already been promulgated by related administrative authorities (Chen et al., 2005; Zhou and Wang, 2005). However, SPWPI still occurred in 2004, which is the most severe event to date. According to the report of the China Environmental Status in 2009, the polluted river-sections accounted for nearly 63% of the total evaluated sections in the Huai River Basin, which ranked the second position in the seven largest river basins of China. The water pollution situation in the Huai River Basin was still very serious, and the system of water pollution control bore a heavy responsibility. The frequent occurrence of SPWPIs has restricted the sustainable development of the socio-economy in Huai River Basin.

Previous studies of water-environment control focused on the control of pollution sources (Hu et al., 2008; Wang et al., 2006; Zhang et al., 2005; Zhang et al., 2010, 2011, 2012, 2013; Zhao et al., 2010, 2012). Hu et al. (2008) assessed the hydrologic alteration at the Wujiadu station and demonstrated the influence of the Bengbu Sluice and all of its upstream dams on the hydrologic regime and eco-hydrological conditions in the Huai River Basin by using Indicators of Hydrologic Alteration and Range of Variability Approach methods. Zhang et al. (2010, 2012, 2013) quantified the impact of water projects on the flow regime and water quality in the upper and middle area of the Huai River Basin by an integrated water quantity and quality model rules. Zhao et al. (2010, 2012) recognized the key regions for restoration of phytoplankton communities in the Huai River basin and assessed the impact of the dam/sluice system on the in stream ecosystem. Zhang et al. (2011c) investigated the major chemical ions of 52 cross-sections from nine different water bodies the Huai River basin in the earlier summer of 2008.

However, the systematic cause analysis of SPWPIs has been ignored. This research belongs to interdisciplinary research involving hydrology and environmental science and has become an urgent and complicated task for the control of water pollution in the Huai River Basin (Xia et al., 2011).

In this study, five SPWPIs (in 1989, 1994, 1995, 2000 and 2004) were selected to investigate their causes. This paper is organized as follows. Firstly, the study area, data source and the method were introduced. Secondly, the variation of meteorology, hydrology, water quality, pollution sources and the operation of dams and sluices was specified during the incidents in the middle and lower regions of the Shaying River. Finally, the formation mechanism of SPWPIs and its influencing factors were defined.

This research was expected to provide scientific and technological support to prevent the specified paroxysmal water pollution incidents, help identify the causes of the deterioration of the water environment, and guide the implementation of water pollution control and ecological restoration in the Huai River Basin.

2. Data and methods

2.1. Research area

The Huai River Basin is located on the north-south border of China (Fig. 1), between the Yangtze River Basin and the Yellow River Basin. SPWPIs mainly occur in the middle and lower reaches of Shaying River and within the upper reaches of Hongze Lake. Shaying River, as the largest tributary of the Huai River, originates from Funiu Mountain in Henan province, and flows through about forty cities in the Henan and Anhui provinces. It has drainage area of 40,000 km² and mainstream of 620 km.

Many water projects have been constructed from the headstream to the lower reach. e.g., Zhaopingtai reservoir, Baiguishan reservoir, Baisha reservoir, Mawan sluice, Luohe sluice, Zhoukou sluice, Huaidian sluice, Fuyang sluice, Yingshang sluice. The regulations of these dams or sluices have changed the flow regime characteristics and pollutant migration mechanisms. Meanwhile, Shaying River is the most seriously polluted tributary, and the pollutant emissions in this basin account for more than 40% of the whole input into the Huai River Basin. Thus the Shaying River is known as an "indicator" of the water environment in the Huai main river. Many SPWPIs were related to the Shaying River (Chen et al., 2005; Zhang et al., 2010), so this area has been selected as the research area in this study.

2.2. Data

The precipitation, runoff, pollution source and water quality monitor data from the five serious SPWPIs (in 1989, 1994, 1995, 2000 and 2004) were collected.

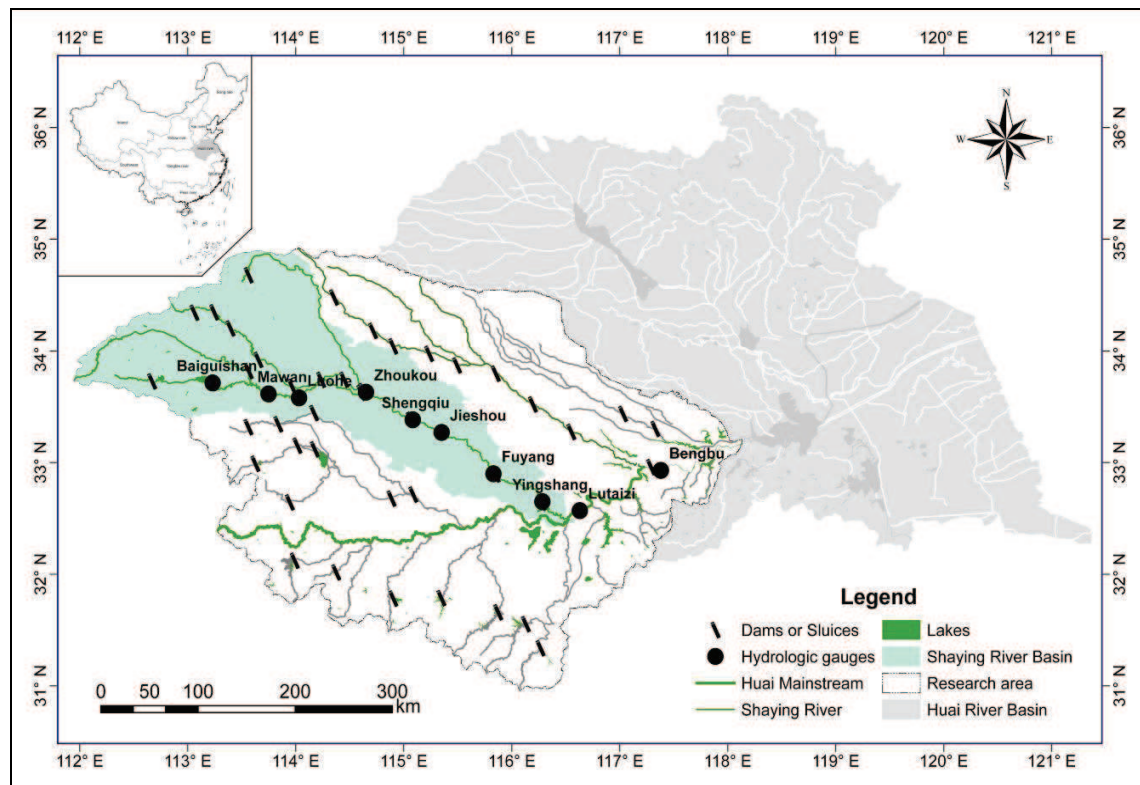


Fig. 1. Research area location

Precipitation and runoff data was collated from the Huai River Water Resources Commission; the pollution sources data and water quality data in the main river cross-sections were selected from the routine monitoring database in the Huai River Water Resources Protection Bureau. The daily precipitation data from the 172 rainfall stations and daily runoff hydrographs of the main gauges (Luohe, Zhoukou, Jieshou, Fuyang, Yingshang, Lutaizi and Bengbu) from upstream to downstream were considered. Currently, the main pollutant sources are industrial and sewage pollution, which accounts for over 70% of the total pollutants (sewage, chemical spill, fertilizer runoff etc.).

The common water quality indices to evaluate the water environment are $\text{NH}_3\text{-N}$ and COD_{Mn} . Thus, the data from these two pollution source indices are summarized at the country scale from the pollution emission monitor data of all the outlets in the research area.

2.3. Method

Daily precipitation data from the 172 stations are interpolated using the spatial analysis module in Arc GIS 9.3 and a runoff hydrograph, where pollution source and water quality monitoring data are overlaid. The spatial and temporal distributions of these factors were analyzed to determine the occurrence time and location of the SPWPIS, and identify the influencing factors. The contents of the research are given below:

(1) Analyze the distribution of the pollution source and evaluate the water pollution situation and its distribution according to the pollution source data at county scale.

(2) Analyze the runoff hydrograph during the water pollution incident occurrence year, evaluate the regulation of dams and sluices and determine the occurrence time and the effect of dam regulation.

(3) Analyze the spatial and temporal variation of the area precipitation during the water pollution incidents, and determine the precipitation conditions which could probably induce the incidents.

(4) Identify the essential conditions causing the incident, including climate change, the amount and distribution of the pollutants and the irrational regulations of dams, etc.

3. Results and discussion

3.1. The spatial distribution of pollutant source

All the emission data of $\text{NH}_3\text{-N}$ and COD in the research area were shown in Fig. 2 at county scale. Most countries have excessive discharges of industrial and sewage pollutants, well beyond the water environmental capacity (pollution limits) of all rivers and lakes, especially in the Hongru River, the Shaying River and the Guo River (Xia et al., 2011).

In the Shaying River basin, pollutants mainly concentrate in the middle and lower streams of the Shaying River and the Jialu River, and the emissions of $\text{NH}_3\text{-N}$ were a little more serious than those for COD.

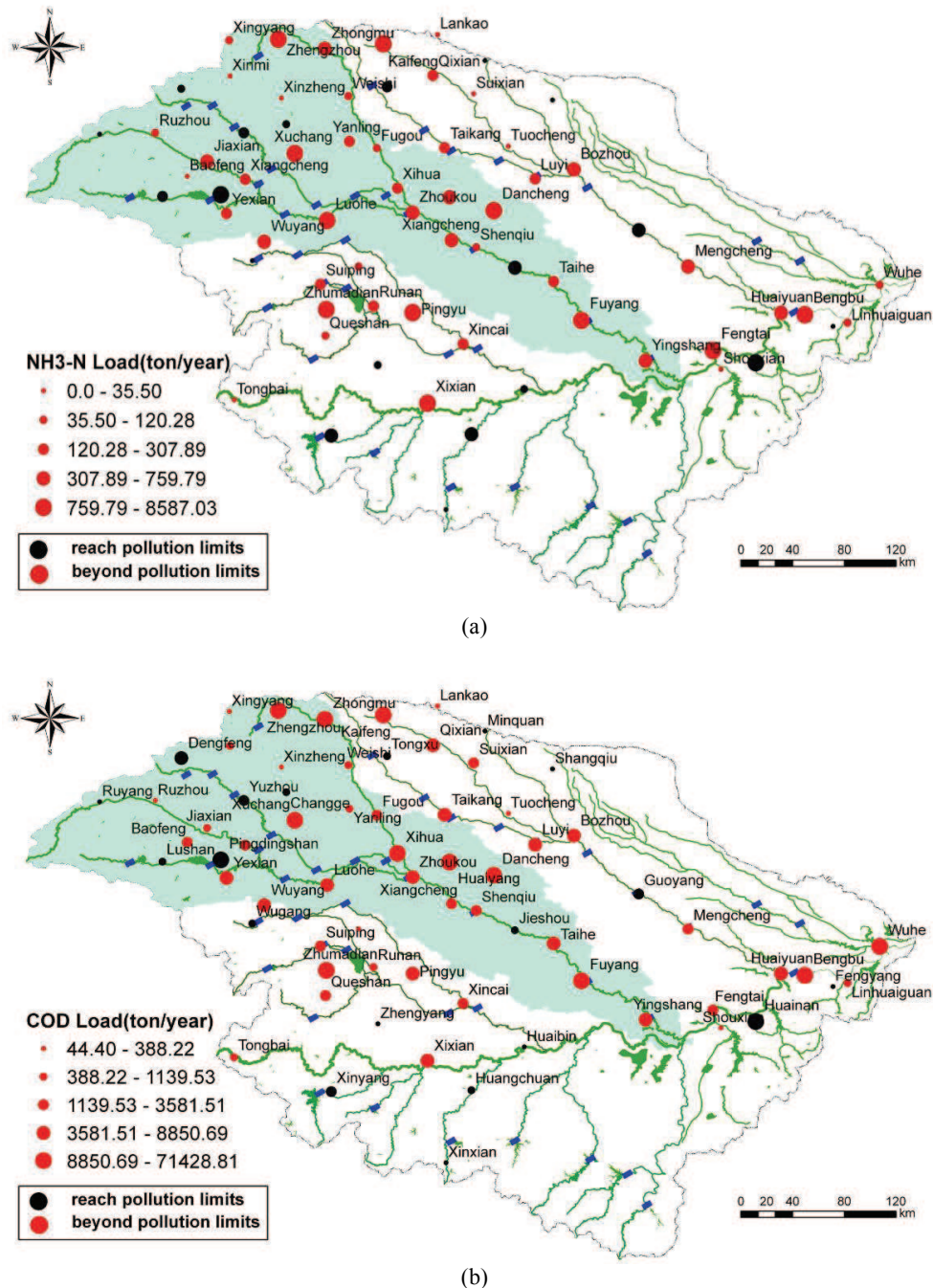


Fig. 2. Annual average main pollutant discharge in research area (NH₃-N (a) and COD (b))

The excessive emissions from pollution sources have directly caused the serious water pollution situation.

The concentrations of NH₃-N and COD before and after the occurrence of the SPWPis were evaluated, and showed that water quality was good in the headstream of Shaying River, while other sluices of Shaying River showed quality was worse than Grade V, especially in the Huaidian, Fuyang and Yingshang sluices (middle and lower reaches of the Shaying River).

The highest concentration of NH₃-N and COD reached 55.6mg/L (Huaidian sluice, 2000) and 348mg/L (Huaidian sluice, 1994), respectively,

which was much worse than Grade V in the water quality standard of surface water (NH₃-N: 2mg/L; COD: 40mg/L). From the Mawan sluice to downstream of Shaying River, there were many pools of high sewage concentration in all the sluices, so the risk of water pollution incident is very high in this area.

3.2. Dispatch analysis of dams and sluices

The daily runoff hydrograph in 1989, 1994, 1995, 2000, and 2004 showed that all of these incidents occurred during the first flooding in pre-flood periods.

Table 1. Water quality at some typical dams or stations before and after water pollution incidents happening

<i>River</i>	<i>Stations</i>	<i>Targets</i>	<i>Time</i>		<i>1989</i>			<i>1994</i>			<i>1995</i>			<i>2000</i>			<i>2004</i>		
				<i>NH₃-N</i>	<i>COD</i>	<i>Grade</i>	<i>NH₃-N</i>	<i>COD</i>	<i>Grade</i>	<i>NH₃-N</i>	<i>COD</i>	<i>Grade</i>	<i>NH₃-N</i>	<i>COD</i>	<i>Grade</i>	<i>NH₃-N</i>	<i>COD</i>	<i>Grade</i>	
Shaying	Baiguishan	II	Before	-	-	-	0.65	15.31	II	0	14.18	I	0	12.47	I	0	10	I	
			After	-	-	-	0.65	15.31	III	0	14.18	II	0	18.14	III	0	13.5	I	
	Mawan	III	Before	1.56	-	III	2.88	111	V+	10.2	64	V+	17.9	83.7	V+	0.43	31	V	
			After	0.06	-	I	1.17	28.66	IV	3.9	44.58	V+	0.21	23.88	IV	0.24	23	IV	
	Luohe	III	Before	-	-	-	1.59	45.44	V+	-	-	-	3.32	42.2	V+	0.1	27.3	IV	
			After	-	-	-	0.46	35.22	V	0.32	22.72	IV	0.2	38.62	IV	0.08	20	III	
	Zhoukou	III	Before	0.05	62.17	V+	1.4	54.81	V+	0.7	71.98	V+	6	49.49	V+	0.98	17.4	III	
			After	0.31	8.18	I	0.6	16.36	III	0.1	37.63	V	0.2	20.45	IV	0.12	22	IV	
	Jieshou	III	Before	-	-	-	14	76.59	V+	-	-	-	12.7	59	V+	8.51	35	V+	
			After	-	-	-	-	-	-	-	-	-	0.33	20	III	0.38	17	II	
	Huaidian	III	Before	2.5	50.4	V+	1.2	245	V+	1.2	348.6	V+	55.6	167.3	V+	13.4	34.8	V+	
			After	3.49	56	V+	0.3	34.8	IV	0.1	19.6	III	0.38	39	V	0.55	17	III	
	Fuyang	IV	Before	5	26.85	V+	18	126.6	V+	36	88.78	V+	16.2	128.2	V+	6.04	53.4	V+	
			After	4	48.22	V+	5	37.26	V+	2	74.53	V+	0.1	15	III	0.17	17.1	II	
	Yingshang	IV	Before	5	49	V+	28	135.5	V+	36	74	V+	11.5	62.5	V+	1.6	83.7	V+	
			After	2.4	23.5	V+	3	21	V+	1.2	25	IV	0.08	22	IV	0.16	17.2	II	
Huai	Lutaizi	III	Before	5	9.5	V+	0.2	3.9	I	0	8.4	I	0.24	8.1	I	0.11	3.3	I	
			After	1	3.9	III	0	4.9	I	0	3	I	0.31	25	IV	0.25	14.2	II	
	Bengbu	III	Before	5	26.4	V+	0.96	23.7	IV	6	20.6	V+	0.14	21.9	IV	0.08	10.2	I	
			After	0.8	11.5	III	0.5	38.7	IV	4	18.7	V+	0.19	14.9	II	0.33	13	II	

Note: The target means the water quality concentration in this station need to reach. Grade I: the national nature water source area (NH₃-N:0.15mg/L;COD:15mg/L);Grade II: primary class drinking waterprotection area (NH₃-N:0.5mg/L;COD:15mg/L);Grade III: secondary class drinking water protection area, sNH₃-N:1.0mg/L;COD:20mg/L).Grade IV: general industrial water supply area NH₃-N:1.5mg/L;COD:30mg/L).Grade V: agricultural water supply area (NH₃-N:2.0mg/L;COD:40mg/L);Grade V+: essentially without any use (concentrations of NH₃-N and COD were greater than the standard of Grade V)(China State Environmental Protection Administration, 2002; Xia et al.,2011). The grade of water quality in each station was depended on the grade of the worst index of NH₃-N and COD.

The dispatch of dams and sluices has had very significant effects on the inter-annual distribution of runoff (Wang et al., 2010; Zhang et al., 2010). The dispatch rules for dams and sluices indicate that in the pre-flood season, the gates are closed for water storage to guarantee water supplies, thus the dispatch of dams or sluices greatly reduced the water discharge. In the flood season, the gates opened and the storage water was discharged rapidly in order to maintain flood safety. Thus, runoff is far more than the annual average flow.

The first flood in 1989 occurred on 7th March. Runoff at each cross-section was only 15–38% of the annual average flow before the flood. During the flooding time, the peak flow of Luohe dam in the middle of the Shaying River reached 177m³/s, about 4.1 times the annual average flow at this cross-section. The peak flow of Fuyang sluice reached 371m³/s, about 2.6 times its annual average flow. At the same time, the peak flow of Lutaizi station in the Huai River reached 1740m³/s, and the discharge of the Shaying River was about 21% of the flow in Huai River. Compared with the annual contribution (18%) of Shaying River's runoff to Huai River in 1989, this flood had little effect on the flow of Huai River.

The dispatch of dams and sluices on flow regime was most obvious in 1994 when the first flood was occurred on 13th July. Runoff at each cross-section was 67–82% of the annual average discharge before the flood. During the flood time, the peak flow of the Luohe dam in the middle stream of the Shaying River reached 854m³/s, about 33 times its annual average flow. The peak flow of the Fuyang sluice reached 696m³/s, about 44 times its annual average flow, while the peak flow of the Lutaizi

station in the Huai River was only 724m³/s, and the total discharge of the Shaying River was about 96 percent of the flow of the Huai River. Compared to the annual contribution (7%) of Shaying River's runoff to Huai River in 1994, this flood significantly affected the flow regime in the Huai River. Obviously, the water quality of the flood discharge also had a direct effect on the water environment of the Huai River.

Like the incident in 1994, the first floods in 1995, 2000 and 2004 occurred on 26th July, 27th June, and 18th July, respectively. Each cross section was nearly dry at the time before the flood, and their runoffs were less than 20% of the annual average discharge. However, during the flood the peak flow of the Luohe dam, Zhoukou sluice, and Fuyang sluices increased sharply and was several or dozens of times their annual average discharge. For instance, it was 25 times the annual average discharge at the Luohe dam, and 14.3 times at the Fuyang sluice in 1995. Meanwhile, the total discharge of the Shaying River was more than 70% of the flow in the Huai River, which was much higher than the annual contribution of the Shaying River's runoff into the Huai River. Therefore, the water quality of the flood is also a key influencing factor on the water environment conditions of the Huai River.

3.3. Temporal and spatial variation of precipitation

The temporal and spatial distribution of precipitation from the end of February to the beginning of March in 1989 showed that it rained from 28th February to 3rd March within the study area.

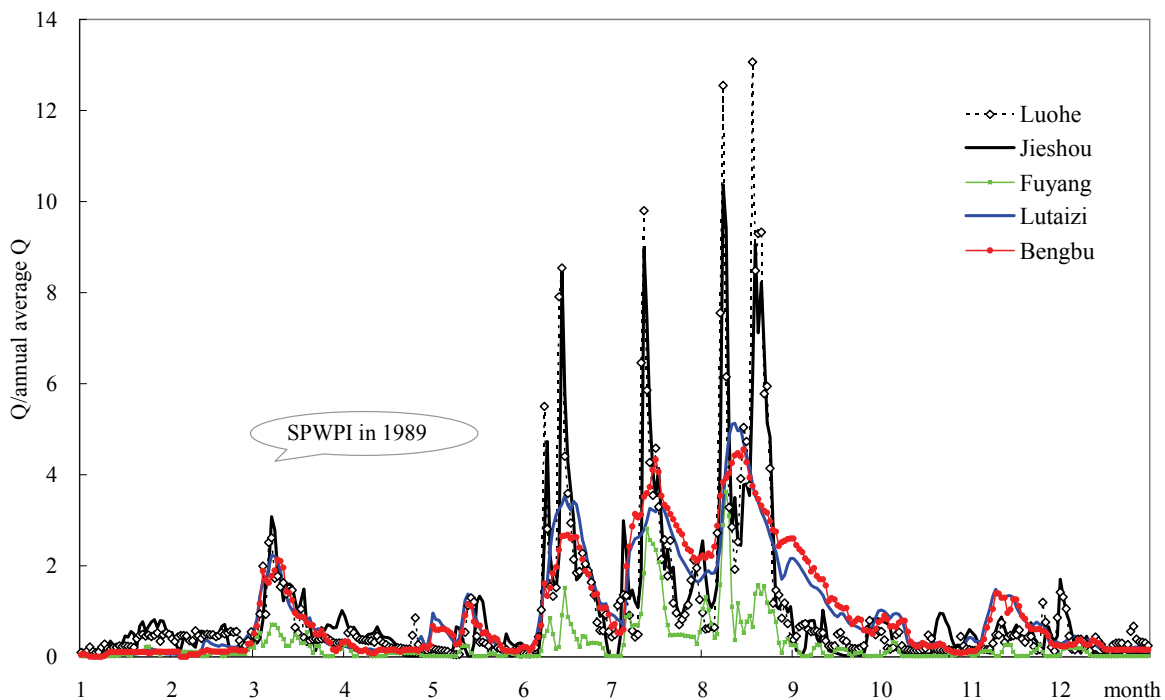


Fig. 3. Daily runoff hydrograph in 1989 at some typical stations

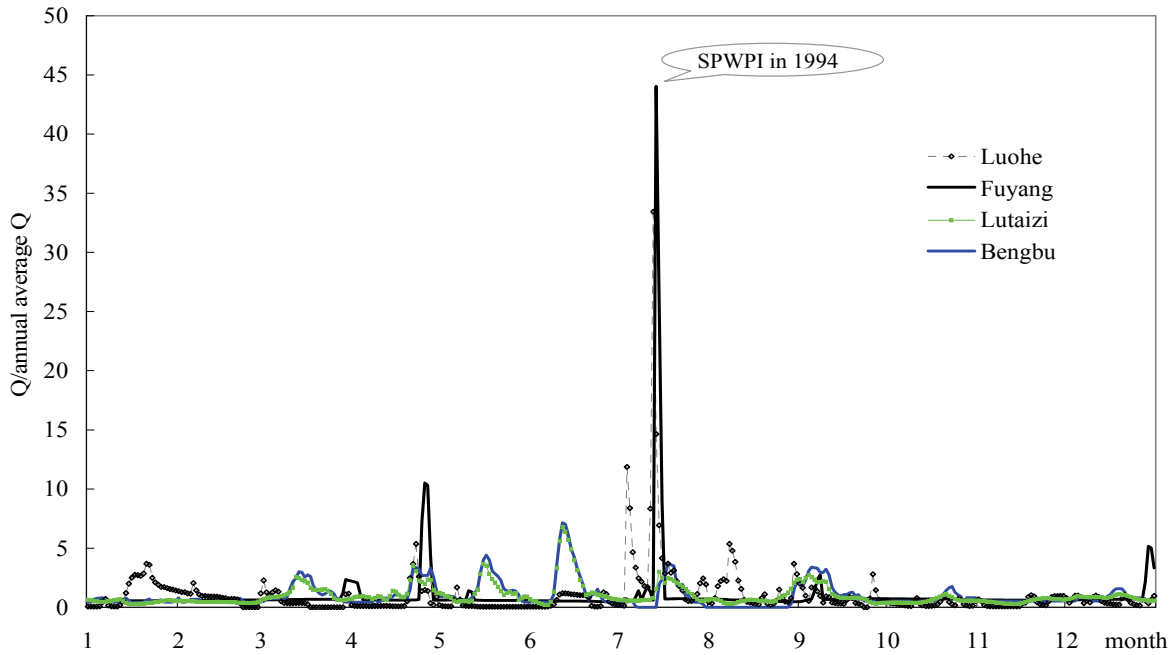


Fig. 4. Daily runoff hydrograph in 1994 at some typical stations

Table 2. Runoff variation at some typical stations in 1989, 1995, 2000 and 2004, respectively

River	Main cross-section	1989		1994		1995		2000		2004	
		time	$Q(m^3/s)$	time	$Q(m^3/s)$	time	$Q(m^3/s)$	time	$Q(m^3/s)$	time	$Q(m^3/s)$
Shaying River	Luohe Dam	3-7	177/43	7-13	854/26	7-26	1200/48	-	-	7-18	59.66/53.08*
	Zhoukou sluice		-		-		-	6-27	1970/205	7-18	2340/124.3
	Jieshou	3-7	306/99		-		-	6-27	1630/213		-
	Huaidian sluice		-		-		-		-	7-19	2360/131
	Fuyang sluice	3-7	371/143	7-14	696/16	7-27	826/58	6-27	1180/243	7-20	30.89/28.90*
	Yingshang sluice		-		-		-		-	7-20	25.15/24.10*
Huai River	Lutaizi	3-7	1740/782	7-15	724/240	7-27	1110/323	6-27	1340/924	7-22	3340/556
	Bengbu sluice	3-7	2070/970	7-18	780/210	7-27	1060/344	6-27	1620/1166	7-22	3580/678

Note: In the column of Q , "-/-", the first number is the flood peak in the incidents, and the last number is the annual average runoff. "*" is the water level and the unit is "m".

Table 3. Runoff contribution of Shaying River to Huai River in 1989, 1995, 2000 and 2004, respectively

The runoff contribution in Shaying River to Huai River (%)	1989	1994	1995	2000	2004
The annual average runoff	18.3	6.6	17.9	26.3	23.6
Flood peak in the incidents	21.3	96.1	74.4	88.1	70.7

Specifically it was light rain on 28th February and 3rd March, moderate rain on 2nd March, with heavy rain in local area and no precipitation from 4th to 8th March. Nonetheless, the SPWPI occurred on 7th March, so this incident had no obvious link with heavy precipitation events.

The SPWPI in 1994 occurred on 13th July. The temporal and spatial distribution of precipitation in the middle of July showed that there were storm conditions over the upstream area of the Shaying River with no rain in the Lutaizi-Bengbu region in the mainstream of the Huai River on 11th July. The storm center moved downwards on 12th July and the rainfall area increased; the storm center moved towards Fuyang in the Shaying River on 13th July,

and the rainfall intensity reduced. The rainfall intensity increased on 14th July when the storm center was located upstream of the Guo River and the Jialu River, which are tributaries of the Shaying River. It can be deduced that the widespread intensive precipitation on 11th and 12th in the upper and middle stream of the Shaying River resulted in the water storage of dams and sluices increasing significantly.

The temporal and spatial distribution of precipitation and the occurrence of the SPWPI showed that the rainfall area was quite consistent with the incident area, and the rainfall was slightly earlier than the incident, so the occurrence of this flood was closely related to the intensive rainstorm.

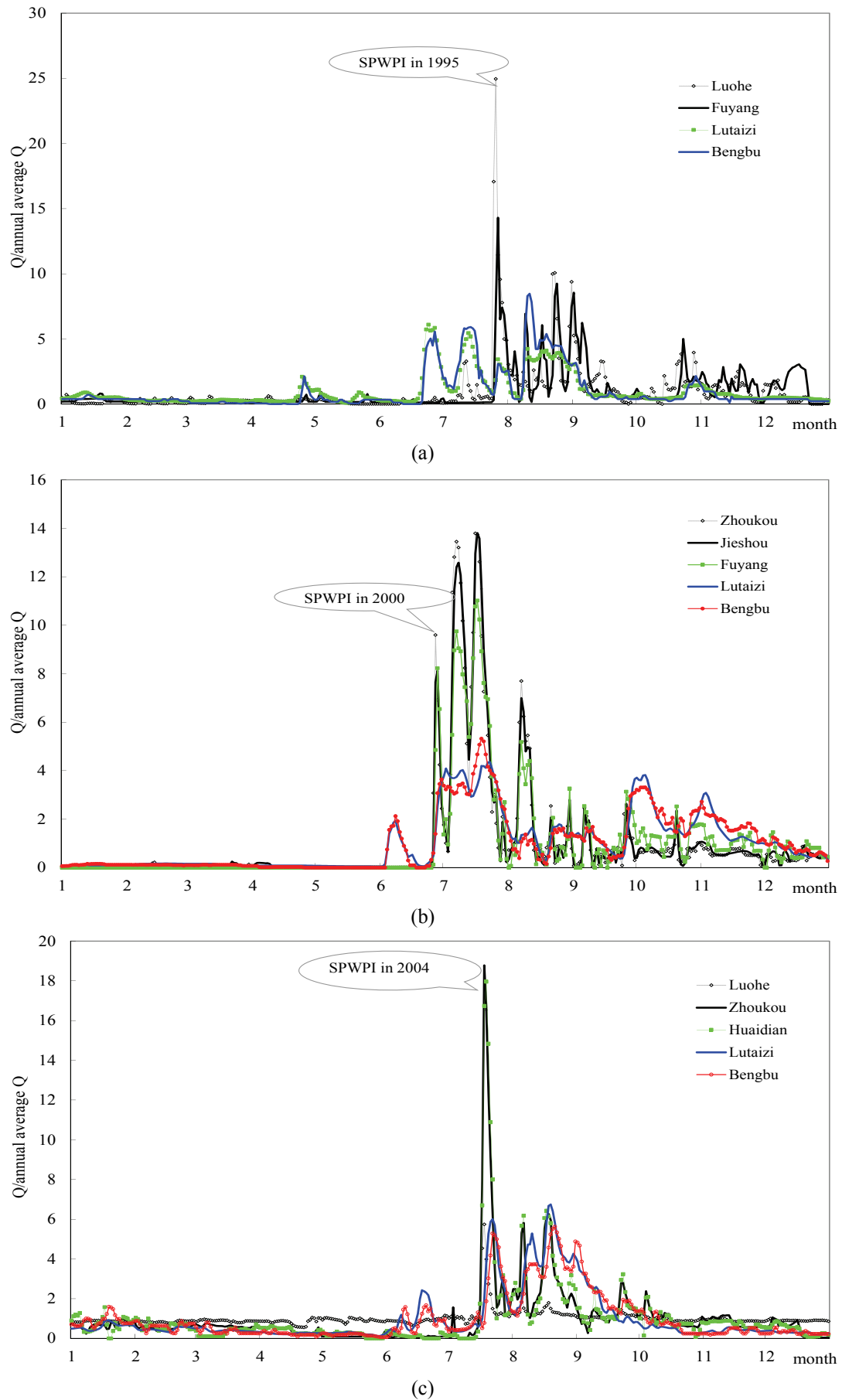


Fig. 5. Daily runoff hydrograph at some typical stations in 1995 (a), 2000 (b) and 2004 (c), respectively

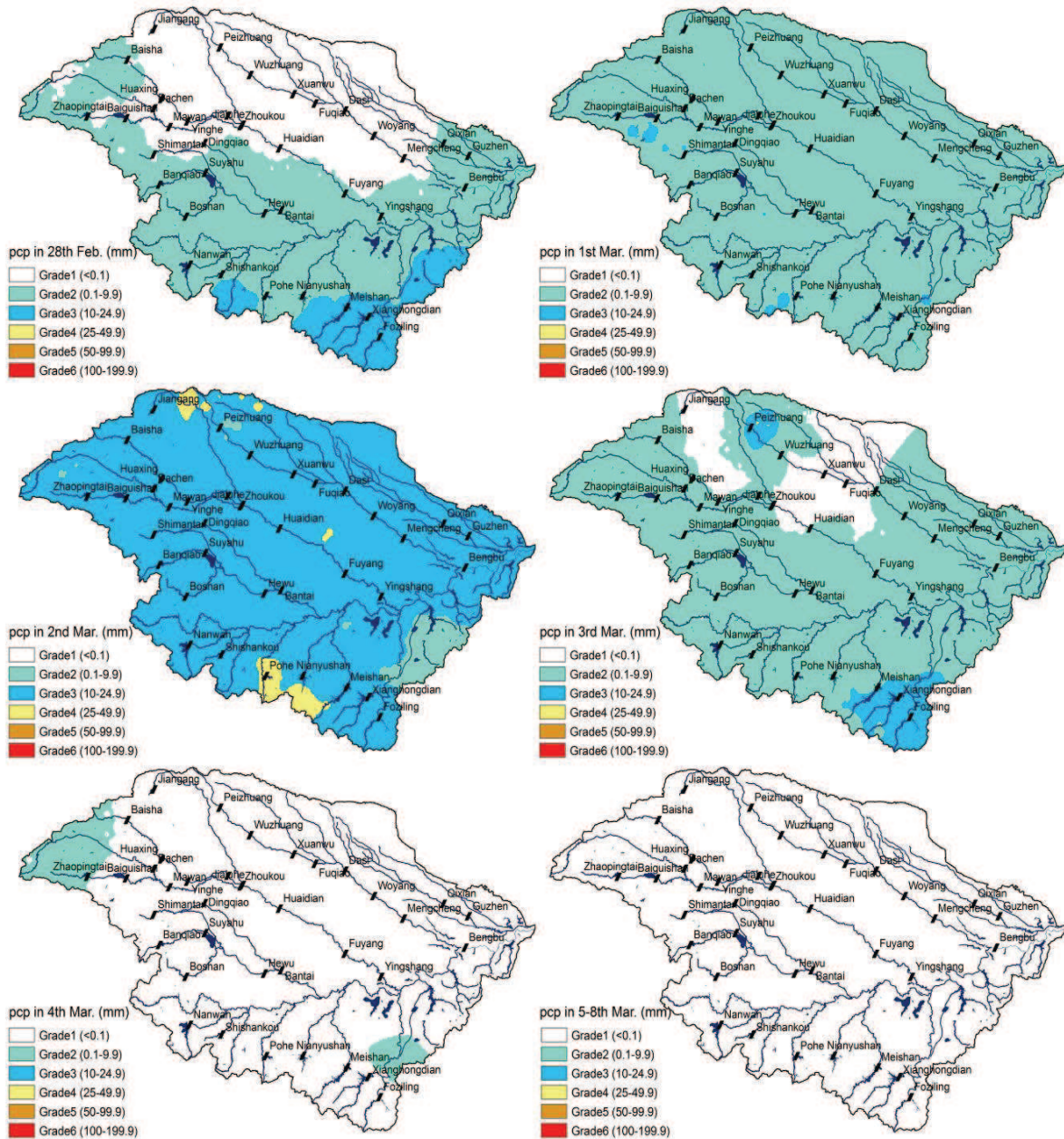


Fig. 6. Daily precipitation variation at middle and upper stream of Huai River Basin from 28th Feb. to 8th March, 1989 (Note: the precipitation intensity classification was according to the national standard issued by China meteorological administration (2008).

Grade 1-No rain: when the daily precipitation rate is <0.1 mm; Grade 2 -Light rain: when the daily precipitation rate is between 0.1 mm and 9.9 mm; Grade 3-Moderate rain: when the daily precipitation rate is between 10.0 mm and 24.9 mm; Grade 4- Heavy rain: when the daily precipitation rate is between 25.0 mm and 49.9 mm; Grade 5- Rainstorm: when the daily precipitation rate is between 50.0 mm and 99.9 mm; Grade 6- Violent rain: when the daily precipitation rate is between 100.0 and 199.9 mm)

The SPWPI occurred around 26th July in 1995, 27th June in 2000 and 18th July in 2004, respectively is similar to 1994. Widespread intensive precipitation occurred from 23rd to 24th July, 1995, and from 24th to 26th June, 2000, with the storm center lying mainly over the upper and middle regions of the Shaying River.

The temporal and spatial distribution of both precipitation and SPWPI showed that the rainfall area was quite consistent with the incident area, with rainfall occurring slightly earlier than the incident. Therefore, it can be deduced that these floods were

closely related to the recent intensive rainstorms.

3.4. Cause analysis of paroxysmal water pollution incident

The analysis of the pollutant discharge condition, dispatch rules of dams and sluices, and the temporal and spatial variation of precipitation during the five paroxysmal water pollution incidents in 1989, 1994, 2000, and 2004, respectively, indicate that SPWPIs usually occurred at the time of the first flooding during the pre-flooding period.

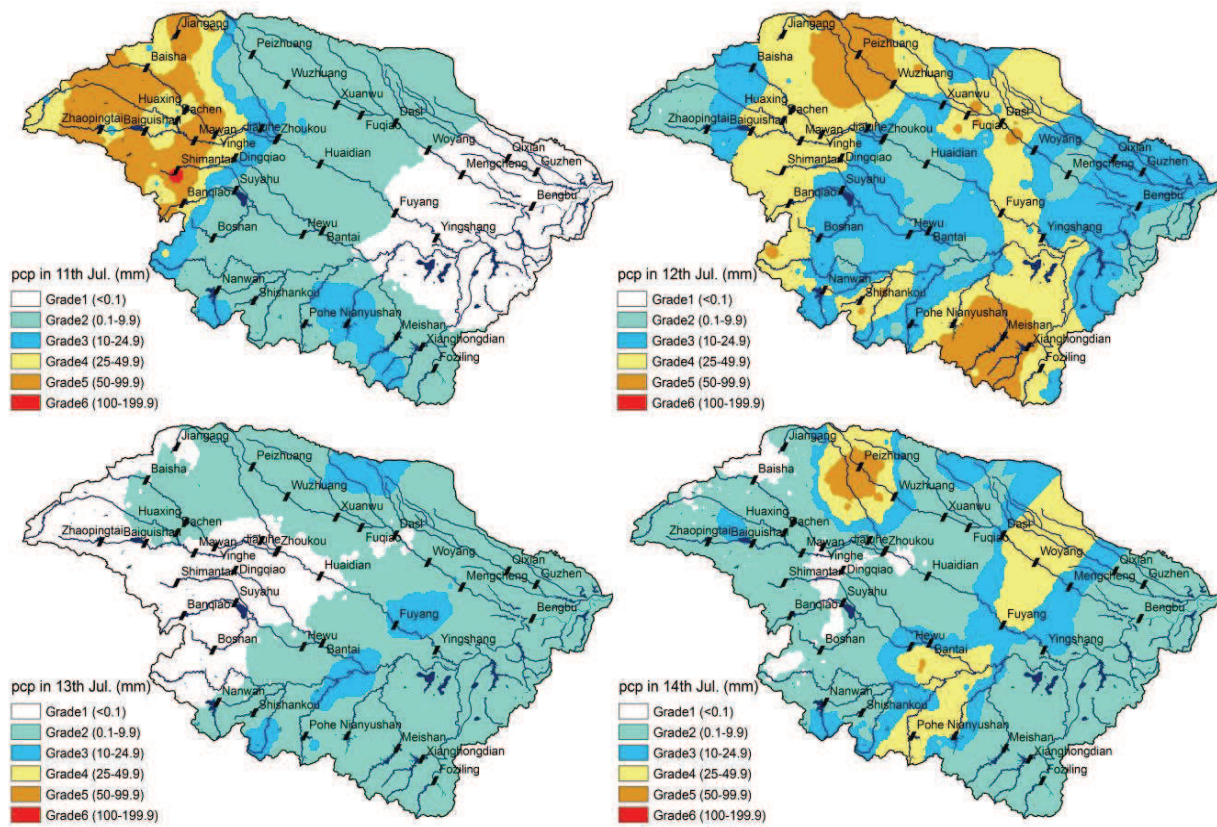


Fig. 7. Daily precipitation variation at middle and upper stream of Huai River Basin from 11th to 14th July, 1994

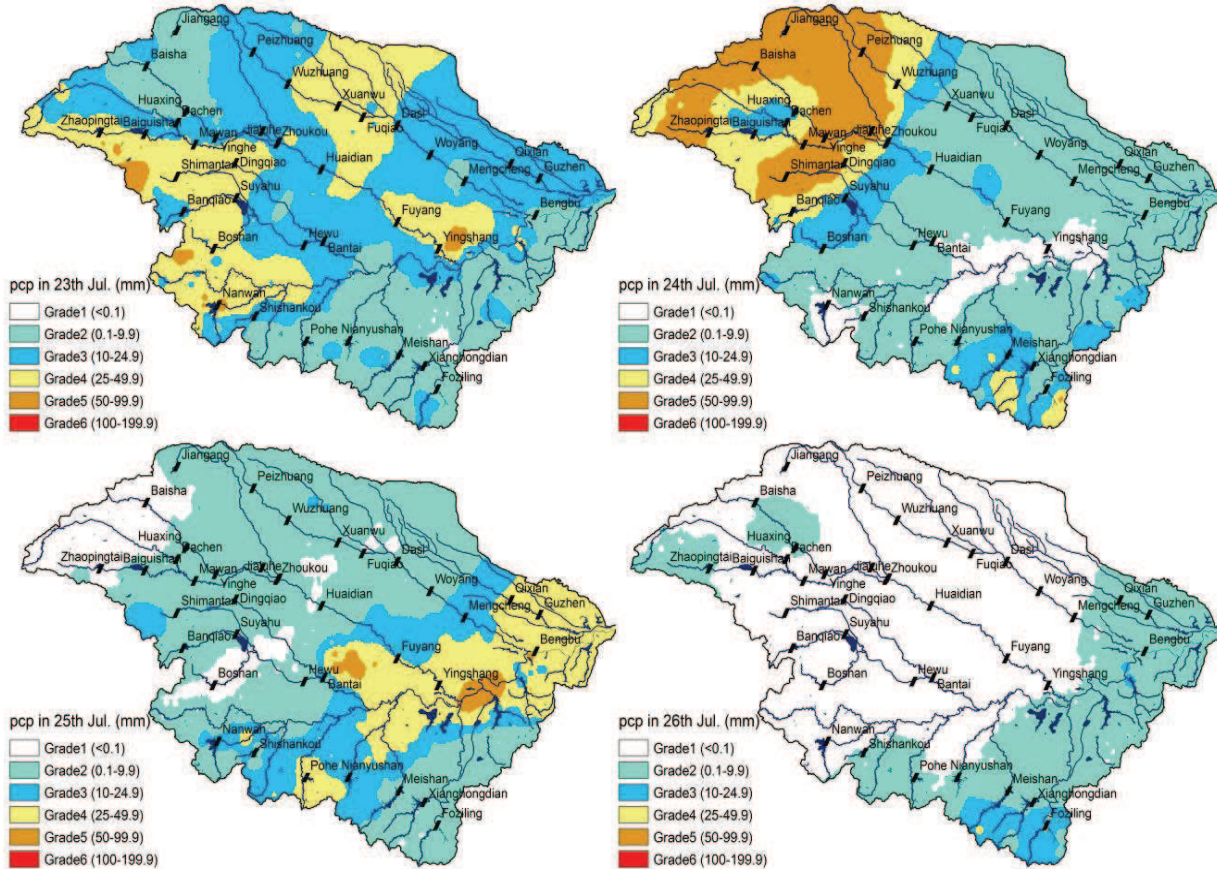


Fig. 8. Daily precipitation variation at middle and upper stream of Huai River Basin from 23th to 26th July, 1995

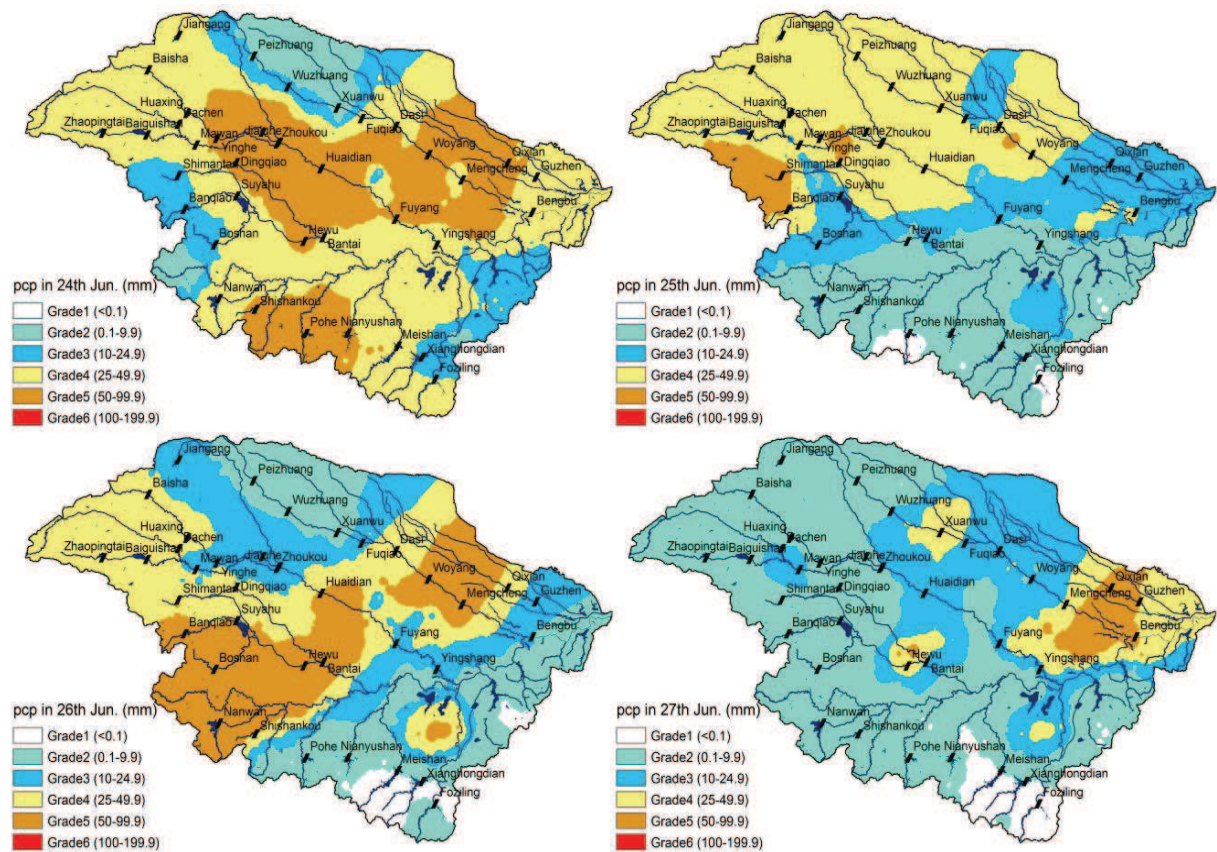


Fig. 9. Daily precipitation variation at middle and upper stream of Huai River Basin from 24th to 27th June, 2000

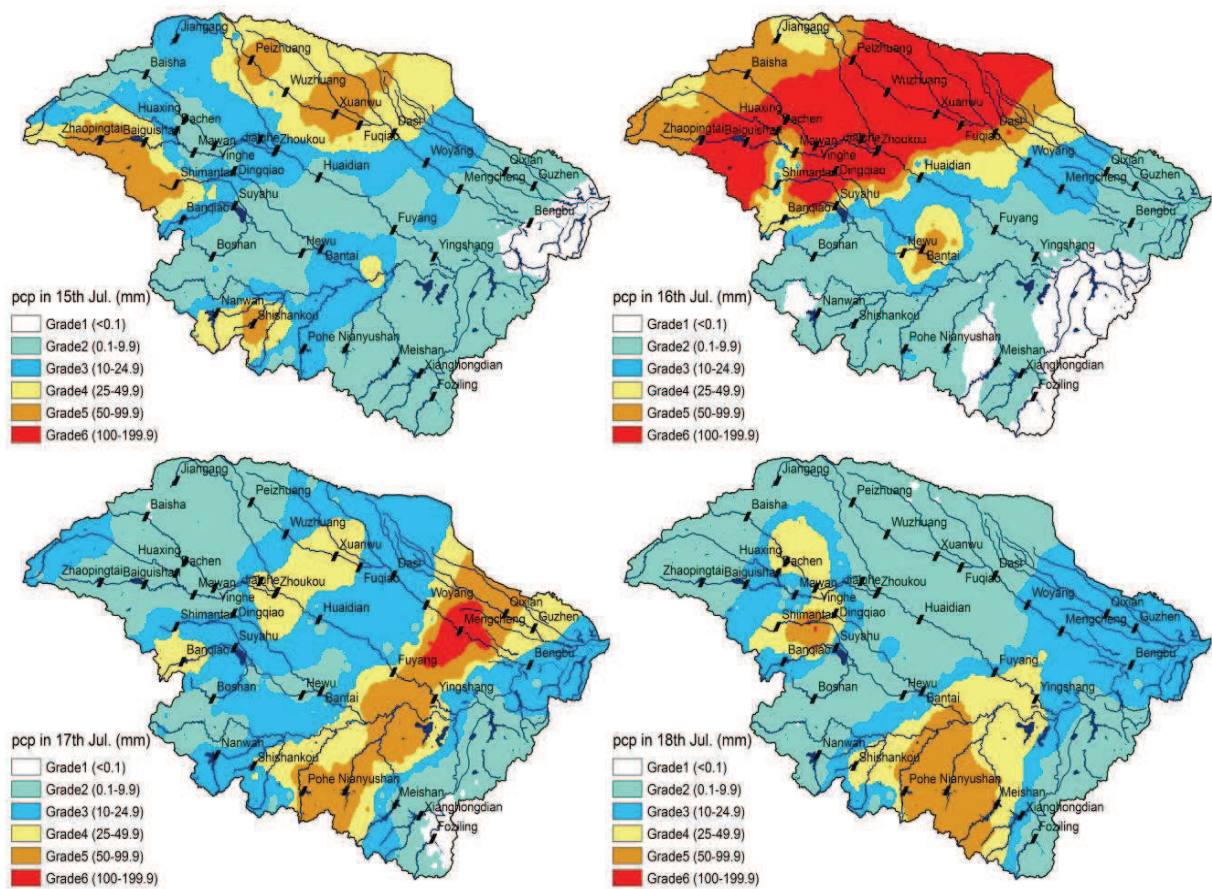


Fig. 10. Daily precipitation variation at middle and upper stream of Huai River Basin from 15th to 18th July, 2004

The excessive emissions of pollutants, excessive amount of dam construction and irrational regulations directly caused the serious pollution of the majority of the upper and down Huai River. Meanwhile, a dozen middle and large sized sluices have been constructed along the Shaying River, such as the Mawan sluice, the Luohe dam, the Huaidian sluice, the Fuyang sluice and the Yingshang sluice. To guarantee water supplies in the dry season, each dam or sluice was closed to store water, so the water volume stored upstream was large but the water quality concentration was rather high.

The rivers were segmented with rather poor connectivity. Therefore, the Shaying River was divided into several huge and highly concentrated pollutant masses. If an upstream flood was coming, the discharged flow of sluices or dams increased sharply for flood control purposes, which was several or dozens of times greater than the average flow, as seen in the incidents in 1994, 1995, 2000 and 2004. The discharged flow of the Shaying River occupied more than 70% of the flow in the Huai mainstream, which is much higher than its annual contribution. Therefore, the high concentrated pollutant discharged from the Shaying River directly impacted the environment and ecology of the Huai mainstream, causing the SPWPI.

The widespread intensive precipitation over the upper and middle Shaying River is an important factor, which directly leads to the incident. The occurrence of the SPWPIs in 1994, 1995, 2000 and 2004 has direct links with the first heavy precipitation before the flood season. The northern regions of the Huai mainstream, which were heavily polluted and intensely regulated by dams and sluices, i.e., the Shaying, Hongru and Guo Rivers, and so on, combined with the widespread intensive precipitation resulted in water storage and caused water levels in dams or sluices to rise rapidly. For instance, during the incident in 1994, the water level at the Luohe dam was 6.5 meters higher than its annual average water level, 2 meters and 1 meter higher at the Fuyang sluice and the Yingshang sluice respectively, meaning that the flooding conditions were extremely serious.

Therefore, intense sluicing for regional flood control resulted in the paroxysmal floods, and thus pollutant incidents occurred, causing SPWPIs. In addition, SPWPIs were more likely to happen if no rain appeared in the Huai mainstream and southern mountainous region. Nonetheless, the paroxysmal intense precipitation is a trigger factor for SPWPIs, as the incident in 1989 occurred in early spring with no apparent links with the intensive precipitation.

4. Conclusions

The damage and effects of SPWPIs in the Huai River Basin are serious. The reduction or elimination of SPWPIs is a crucial task for water resources management and environmental

governance in the Huai River Basin. Exploring the formation mechanism of SPWPIs and identifying its causes is a fundamental and urgent scientific task. The analysis of the pollutant discharge conditions, dispatch rules of dams and sluices, and the temporal and spatial variation of precipitation during the five SPWPIs in 1989, 1994, 2000, and 2004, respectively, were carried out. The results indicate that the SPWPIs mainly occurred at the first time of flooding during the pre-flooding period.

The excessive emission of pollutants, excessive dam construction and irrational regulations caused the accumulation of pollutants upstream of the dam, and directly induced the incidents. Moreover, the first widespread intensive precipitation during the pre-flooding period is a trigger factor for SPWPIs, which directly leads to the flood discharge of dams and sluices with high concentrations of pollutant from upstream to downstream, and thus SPWPIs occurred, such as in 1994, 1995, 2000 and 2004.

To prevent SPWPIs, it is recommended that: (1) the control of pollution sources should be strengthened, and the total pollution loading should be reduced, especially in the middle and upper streams of the Huai River Basin, such as the Zhoukou, Fuyang, Huaidian, Yingshang, and so on; (2) the integrated dispatch of water quantity and quality of dams or sluices should be applied. The routine or emergency dispatch of dams and sluices for SPWPIs should be worked out scientifically. The routine dispatch should consider water safety between the upstream and downstream, pollutant source discharge etc., and guarantee the environmental flow of every dam and sluice to avoid pollutant accumulation in dams or sluices.

An emergency dispatch should consider the upstream rainfall distribution and intensity, pollutant concentration, etc., prolong the pollutants' discharging time and avoid intensive sluicing. Meanwhile, the integrated dispatch of water quantity and quality of dams and sluices at the north of the Huai mainstream and southern mountainous region should be taken into consideration; (3) real-time monitoring of water quantity and quality at streams where SPWPIs frequently occurred should be strengthened, especially focusing on river regimes and water environmental changes in order to provide basic data for dams and sluices' dispatch rules; (4) relative studies should be further strengthened, by the simulation and forecasting of water quantity and quality, integrated dispatch of water quantity and quality, environmental flow etc., which can provide scientific and technological support to prevent SPWPIs.

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ANAEROBIC BIOREMEDIATION OF PAH-CONTAMINATED SOIL: ASSESSMENT OF THE DEGRADATION OF CONTAMINANTS AND BIOGAS PRODUCTION UNDER THERMOPHILIC AND MESOPHILIC CONDITIONS

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Abstract

The degradation of polycyclic aromatic hydrocarbons (PAHs) including fluorene, phenanthrene, anthracene, fluoranthene and pyrene were investigated under thermophilic and mesophilic anaerobic-methanogenic conditions. By using central composite design, the impact of PAH concentration and soil to inocula ratio were systematically studied for their influence on PAH removal and biogas production. During the first 30 days, PAH concentration decreased in all samples indicating that the inocula used were able to biodegrade the contaminants; although an inhibition effect was initially observed in biogas production. Phospholipids fatty acids analysis was used to monitor the microbial communities present during the process. These communities were more complex in samples containing moderate to high PAH contamination concentrations. After 50 days, the concentration of PAHs increased in the majority of samples indicating possible reversed biotransformation of these compounds.

Key words: anaerobic digestion, central composite design, PAH-contaminated soil, phospholipids fatty acids, thermophilic/mesophilic conditions

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1. Introduction

Soil contaminated with polycyclic aromatic hydrocarbon (PAHs) is a global environmental problem that is continuing to increase because these compounds are widely present in many substances used as part of modern life (Agarwal, 2009). Warnings about the dangers and potential side effects of PAHs have motivated researchers to investigate their bioremediation and detoxification. It is well known that, for many organic contaminants, aerobic treatments are more efficient and widely used than

anaerobic ones because of their broader catabolic range (Cajthaml et al., 2002). However, aerobic processes are not the only options that need to be considered because different types of contaminants can be present for which such processes are difficult to apply. High number of materials contaminated with PAHs could be treated by using anaerobic processes (Popescu et al., 2009; Soceanu et al., 2009), and therefore it is necessary to understand their fate under these conditions, as well as understand if anaerobic treatments could be applied as a biological alternative process.

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Although anaerobic bioremediation of PAH-contaminated soil has been investigated under a number of different conditions relatively little is still known and more research is necessary (Zhang et al., 2000). Recently, various electron acceptors have been used for the anaerobic bioremediation of different compounds such as hydrocarbons (Callaghan et al., 2006; Dionisi et al., 2006; El-Hadj et al., 2006). Evidence of anaerobic degradation of various PAHs have been reported: phenanthrene and fluorene have been degraded by sulphate-reducing bacteria (Coates et al., 1997) and under nitrate-reducing conditions (Eriksson et al., 2003), and iron-reducing and methanogenic conditions promote the degradation of similar compounds (Chang et al., 2002, 2006; Meckenstock et al., 2004; Sayara et al., 2010). It is worth mentioning that a gradient of contaminant concentrations are found in different contaminated matrices, and these concentrations vary from low, such as wastewater sludge ($\mu\text{g/kg}$, dry matter (DM)), to high, such as soils or sediments (g/kg , DM) (Chang et al., 2003, 2008; Christensen et al., 2004; Trably et al., 2003).

Anaerobic digestion under methanogenic conditions can be carried out under different temperature including mesophilic (37°C) and thermophilic (55°C) regimes (De Baere, 2000). However, mesophilic treatments are considered more economical because less energy is required. As a result, most anaerobic full-scale plants work under mesophilic conditions (Ferrer et al., 2008) even though thermophilic treatments have a higher biogas production rate because of the associated faster reaction rates (Cecchi et al., 1991). Accordingly, the study of these two different treatments to gain a full understanding of the mechanisms and behavior of this process is recognized as an alternative source for renewable and clean energy.

In a normal start-up of a batch anaerobic digester a certain amount of inoculum needs to be added together with the substrate to be digested to generate the required conditions and microorganisms needed to start the biological reactions (Liu et al., 2009). Theoretically, the degradation of organic matter including PAHs can be promoted by increasing the density of microbial activity either by favorable conditions or by increasing the amount of microorganisms present. Equally, the adaptability of the introduced microorganisms is also crucial for promoting the digestion process (Fernández et al., 2005). Consequently, the determination of the ratio between the treated material and inoculum is of great importance. In this regard, the minimum amount of inoculum required to provide sufficient activity with the maximum load of organic material is considered to be crucial for process design. The role of anaerobic degradation for PAH-contaminated soil is an area in which little work has been reported. To our knowledge, there is a lack of information about the bioremediation of PAH-contaminated soil under strict methanogenic-anaerobic conditions. To date, there have been no reports of the behavior of such

processes under various temperatures, and no information is available about the influence of the main factors that typically affect the process such as contaminant concentration and soil to inocula ratio.

Hence, the objective of the present study was to comparatively assess the process performance under different operating conditions by using two different types of inoculum requiring different temperature: one thermophilic and one mesophilic. Moreover, two main controlling factors such as the PAH concentration and the soil to inocula ratio were evaluated to assess their effect on the PAH degradation rate. The biogas production was measured as an indicator of process activity, whereas PAH degradation was evaluated by measuring the concentration decrease and the production of biodegradation metabolites using advanced techniques. Also, phospholipid fatty acid (PLFA) analysis was used to determine the evolution of the microbial communities present in each sample. In both the thermophilic and mesophilic case the experiments were systematically carried out by using an experimental design technique considering the different levels of the studied factors, to allow for statistical validation of the results obtained.

2. Experimental

2.1. Soil

The soil used in this study was an uncontaminated soil classified as sandy loam soil. It was collected from the surface horizon (0–30 cm) of an agricultural field located in Prades (Tarragona, Spain). The soil was air-dried and then sieved (2 mm) to remove any debris and kept at 4°C until use. The soil texture consisted of 73.4% sand, 18.6% silt and 8% clay. No PAHs were detected in the soil before being used for experimental purposes. Other properties of the soil are shown in Table 1.

2.2. Contaminants

Fluorene, Phenanthrene, Anthracene, Fluoranthene and Pyrene, all of 98–99% purity, were selected as contaminants in order to evaluate their degradation under anaerobic methanogenic conditions. These compounds were obtained from Sigma-Aldrich (Barcelona, Spain). These five PAHs are included on the list of the 16 USEPA priority pollutants.

The weight percentage of each compound as part of the total PAHs concentration (ΣPAHs) was 33, 31, 10, 22 and 4%, respectively. These percentages were chosen to simulate a real creosote sample the percentages of which were determined following fractionation of a commercial creosote sample (Creosote lot: 42-13B, Chem Service, Sugelabor, Spain) in our laboratory by using the method 3611B of the USEPA, in which the volatile part was ignored. The PAHs were mixed in the appropriate proportions to create a stock solution.

This stock solution was used to spike the soil to obtain the desired concentration according to the experimental design range (0.1–2 g/kg, DM) measured as the total concentration of the five PAHs.

2.3. Anaerobic inocula

In this study, two types of inoculum with different optimal temperatures, thermophilic (55°C) and mesophilic (37 °C), were used. The mesophilic-anaerobic inocula were obtained from the digested effluent of an anaerobic digester after the solid-liquid separation in a waste treatment plant (Barcelona, Spain). The inoculum contained 10.02% of total solids, which is composed of the entire microbial consortium involved in the anaerobic digestion process, together with some difficult to degrade or inert solids. The thermophilic inoculum was obtained from a thermophilic treatment plant (Terrassa, Spain). The thermophilic inoculum was filtered through a 4 mm sieve to remove some big parts of the feedstock and 11.8% total solids remained. In both cases the treatment plants are fed with the source-selected organic fraction of municipal solid wastes. The two inocula were kept separately in plastic containers with a gallon capacity under strict anaerobic conditions and incubated in water baths at 37°C and 55°C for about two weeks before use to remove any biodegradable materials. No contamination by PAHs was detected in the inocula prior to the experiments. Other characteristics of the inocula are presented in Table 1.

2.4. Experimental system

Experiments with both inocula were performed in triplicate by using sealed 1-L bottles (Traveller SIGG®, Spain) as reactors. They were tightly sealed and equipped with a ball valve that can be connected to a digital manometer to determine the pressure of biogas produced. The contaminants were prepared in a stock solution (5 g total PAHs in 500 mL dichloromethane) and used to spike the soil at different concentrations (0.1–2 g/kg total PAHs; approximately 300–6000 mg chemical oxygen demand (COD)/L) determined according to the experimental design technique.

The solvent was allowed to evaporate at room temperature. Next, the soil and inoculum were mixed together based on the dry weight fraction at different ratios ranging from 0.2:1 to 5:1 (w/w, soil/inoculum). As inoculum and soil are different in their total solids content, distilled water was added to the samples to correct for this and ensure the same total solids content for both. Thus, all samples had the same amount of total solids equal to that corresponding in each inoculum (11.8 and 10.02%). All the bottles were then tightly sealed and purged several times with compressed nitrogen gas to ensure anaerobic conditions (Ponsá et al., 2011) before being incubated under strict anaerobic static conditions. The mesophilic samples were incubated in a

temperature-controlled chamber at 37°C, and the thermophilic samples were incubated in an oven adjusted to 55°C. The total experimental time was set to 50 days in line with previous experiments (Sayara et al., 2010). After 30 days one sample from each set of experimental conditions was removed from the incubator to evaluate the process behavior. The remaining samples (in duplicate) were left for the full 50 days. A blank experiment (in triplicate) with only inoculum was used to evaluate the baseline of biogas production by an endogenous matter. These samples did not contain any additional nutrients or organic matter. All the results are expressed as the average measured after 30 and 50 days.

2.5. Analytical methods

2.5.1. Determination of biogas and analysis

The production of biogas was followed and determined quantitatively by measuring the pressure increase in the headspace of the sample bottle by means of a SMC (ISE30) Pressure Switch manometer (1 MPa, 5% accuracy). The quantity of the produced biogas in each sample was determined by subtracting the biogas produced by the inoculum (blank experiment) from that produced in the sample. Because it is crucial to be able to accurately determine the differences between the production of biogas from the inoculum and the PAH experiments, the inoculum was maintained under anaerobic conditions for 15 days prior to use to remove the biodegradable organic matter and to reduce biogas production owing to endogenous activity (Ponsá et al., 2011). The net value of biogas produced was calculated and expressed under normal conditions (0°C and 1 atm). Biogas analysis, particularly the CH₄ and CO₂ contents were determined by using a gas chromatograph (GC 5890 Capillary Hewlett Packard) as described by Sayara et al. (2010).

2.5.2. PAHs analysis

To determine the concentration of PAHs after 30 and 50 days of incubation, the contents of the sample bottles were dried by using a lyophilizer (Benchtop 5L, Virtis Sentry, NY). Lyophilized samples were extracted by using an ASE 200 System (Dionex, Voisins-le-Bretonneux, France). The extraction cell (11 mL) was loaded in an oven and extracted with hexane-acetone (3:1, v/v). The cell was heated (150 °C, 7 min) and subsequently extraction took place at 150 °C under 103.4 bar for 5 min. The cell was then flushed with fresh solvent (60% of total cell volume) and finally the solvent was purged from the cell with nitrogen gas for 60 seconds. For each sample the extraction cycle was performed three times.

The resulting organic extracts were collected in 40 mL vials, dried under vacuum at room temperature and finally dissolved in acetonitrile for subsequent analysis. Reverse phase high-performance liquid chromatography analyses were performed by using a system consisting of a 2695

Separations Module (Waters, Milford, MA) equipped with a LiChroCart column filled with LiChrospher® PAH (250 x 4 mm; particle size 5 µm; pore size 150 Å; Merck, Darmstadt, Germany), a 2996 diode-array detector and 2475 fluorescent detector (Waters, Spain).

Separation of the PAHs was achieved with a gradient program, by using a mixture of methanol:acetonitrile (1:1 v/v, solution A) and Milli-Q water. After 5 min of isocratic elution with 70% of solution A, the eluent was changed slowly to be 100% solution A over 15 min and maintained constant for the following 20 min. PAHs were identified by using UV spectrophotometry and comparison of retention times to commercially available standards (Dr. Ehrenstorfer, Augsburg, Germany). The concentrations of the five PAHs were calculated according to the USEPA method 610.

The compounds were quantified with the fluorescent detector under excitation/emission conditions: phenanthrene and anthracene at –250/390 nm; fluorene, fluoranthene and pyrene at –280/340 nm. Calibration curves with the standards were prepared over a linear range (0.1–10 µg/ml) for each compound, and the recovery rate was approximately 95%.

2.5.3. Metabolite identification

Samples that had been previously extracted (See section 2.5.2) were analyzed by using gas chromatography (Agilent HP 6890 Series II) coupled to a mass selective detector under electronic impact ionization (Agilent HP 5973) with a HP5-MS (30 m x 0.25 mm x 0.25 µm; Agilent, Spain). The operating conditions of the chromatograph were as follows: injector (splitless 1 min) 320°C, injection volume 1–3 µl (depending on the sample), oven temperature: 50°C (1 min), rate 7°C/min, final temperature 320°C with helium as carrier gas at 0.7 ml/min. The detector remained in solvent delay mode for 3.2 min and the mass range measured was 40–400 (m/z). The products detected were identified by comparing the mass spectral data to the Wiley 7® library.

2.5.4. Volatile fatty acids

The total volatile fatty acid composition (acetate, propionate, *iso*-butyrate, *n*-butyrate, *iso*-valerate, *n*-valerate; (g/L)) was determined by using gas chromatography (GC). Samples were centrifuged for 10 minutes (10⁴ rpm) then filtered through to remove any solid particle (0.25 µm). Known volumes of the filtrates were mixed equally (1:1, v/v) with pivalic acid as standard, before analysis by GC. Samples (1 µl) were injected into the GC (GC 5890 Capillary Hewlett Packard) equipped with a flame ionization detector (280°C) and a splitless injector (260°C). A HP-Innowax column (Crosslinked polyethylene Glycol; 30 m x 0.53 mm x 1 µm; Agilent) was used.

The temperature was maintained at 80°C for 1 min before increasing at a rate of 5°C/min until 150°C and then at 20°C/min until 230°C was attained.

2.5.5. Evaluation of the bioavailability of PAHs

The bioavailable fractions of PAHs were estimated by using sequential supercritical fluid extraction (SFE) (Cajthaml and Šásek, 2005). The extraction was performed with a PrepMaster extractor (Suprex, Pittsburgh, USA) equipped with a VaryFlow restrictor operating at 40°C with a downward stream of carbon dioxide (5.5 SFE/SFC, Supercritical fluid chromatography and extraction system, Messer Technogas, Prague, Czech Republic).

The samples (1 g, dry basis) were extracted at 50 °C and 200 bar. Each extraction was carried out in duplicate and the compounds were collected after 5, 10, 20, 40, 60, 80, 120, 160, and 200 min. SFE represents a desorption model that generally assumes that the extraction is controlled by two rate constants differing in orders of magnitude (Williamson et al., 1998). The “F fraction”, which represents the rapidly desorbed fraction of the target chemical from soil, is usually assumed to be representative of equilibrium release conditions, and the next, more slowly released, portion is considered to be kinetically rate-limited. The chemical release data is then modeled by an empirical two-site model, consisting of two first-order equations (Eq. 1):

$$S_t = F S_0 \exp(-k_1 t) + (1 - F) S_0 \exp(-k_2 t) \quad (1)$$

where: S_t is the pollutant concentration remaining in the soil after time t ; F is the fraction of chemicals that is rapidly released; S_0 is the original concentration of the pollutant in soil; k_1 and k_2 are the first order rate constants. Prism version 5.0 (GraphPad, USA) was used to calculate the F values according to Eq. (1).

2.5.6. Quantification of microbial biomass

Samples for PLFA analysis were extracted by using a mixture of chloroform, methanol and phosphate buffer (1:2:0.8; v/v/v). LiChrolut Si-60 solid-phase extraction cartridges (Merck, Whitehouse Station, NJ) were used for the separation of the extracts and phospholipid fractions were subjected to mild alkaline methanolysis (Šnajdr et al., 2008). Gas chromatography-mass spectrometry (GC-MS) was used for analysis of the free methyl esters of phospholipid fatty acids (450-GC, 240-MS ion trap detector, Varian, Walnut Creek, USA). The GC instrument was equipped with a split/splitless injector and a DB-5MS column (J&W Scientific, Folstom, 60 m, 0.25 mm, 0.25 µm film thicknesses) was used for separation. The temperature program started at 60 °C and was maintained for 1 min in splitless mode.

Then the splitter was opened and the oven heated to 160 °C at a rate of 25 °C min⁻¹. The second temperature ramp reached 280 °C at a rate of 2.5 °C min⁻¹ and this temperature was maintained for 10 min. The solvent delay time was set to 8 min. The transfer line temperature was set to 280 °C. Mass spectral data were recorded under electron impact at 70 eV, mass range 50–350 amu. Methylated fatty acids were identified according to their mass spectra and quantified by using their individual chemical

standards (Sigma-Aldrich, Prague, Czech Republic and Matreya LLC, Pleasant Gap, USA).

Fungal biomass was quantified based on 18:2 ω 6,9 content, bacterial biomass was quantified as a sum of i14:0, i15:0, a15:0, 15:0, i16:0, 16:1 ω 7, 16:1 ω 9, 16:1 ω 5, 10Me-16:0, i17:0, a17:0, cy17:0, 17:0, 10Me-17:0, 18:1 ω 7, 18:1 ω 9, 10Me-18:0 and cy19:0. Biomass of Gram positive and Gram negative bacteria were estimated by using concentrations of i14:0, i15:0, a15:0, 15:0, i16:0 and 16:1 ω 7, 18:1 ω 7, 16:1 ω 5, cy19:0 cy17:0, respectively. To evaluate the anaerobic PLFA markers the quantities of cy19:0, cy17:0 and 18:1 ω 9 were used (Oravec et al., 2004; Sampedro et al., 2009; Šnajdr et al., 2008).

2.6. Experimental design and statistical analysis

The effect of two factors ($k = 2$): the PAHs concentration (x_1) and the soil to inocula mixing ratio (x_2), on the bioremediation of PAHs-contaminated soil under anaerobic conditions were systematically studied by using the central composite design (CCD). More details about the experimental design technique and its application can be found and reviewed elsewhere (Deming and Morgan, 1987; Sayara et al., 2010). The design matrix is presented in Table 2, in which the coded and actual values of the two independent variables (x_1 and x_2) and the actual response of each combination regarding the biodegradation percentage (Y_D) and the biogas production (Y_G) are reported.

In total, nine experiments (in triplicate) were carried out according to CCD principles. Control samples, containing only the corresponding inoculum were also carried out. Statistical analysis was performed for all the variables by using the Sigmaplot® 8.0 software package (Systat Software Inc, San José, USA) and according to the statistics recommended for CCD (Deming and Morgan, 1987).

3. Results and discussion

3.1. Response surface and statistical analysis

CCD was applied to study the process behavior under different variables. The degradation (D) percentage (%) and the biogas (G) production (L kg⁻¹ TS) after 30 and 50 days were selected as functions to be optimized along with their parameters to represent the response of the process. Second order models for each variable are illustrated in Eqs. (2–9)

under thermophilic (T) and mesophilic (M) conditions:

$$Y_{TD30} = 51.9 + 23.28x_1 - 6.69x_1^2 - 0.69x_2^2 - 1.9x_1x_2 \quad (2)$$

$$Y_{TD50} = 32.14 + 25.09x_1 + 6.62x_2 - 5.8x_1^2 - 2.18x_1x_2 \quad (3)$$

$$Y_{TG30} = 3.62x_1 - 7.03x_2 + 3.1x_1^2 + 1.7x_2^2 - 2.4x_1x_2 \quad (4)$$

$$Y_{TG50} = 8.18 + 7.4x_1 - 11.5x_2 - 0.75x_1^2 + 1.9x_2^2 \quad (5)$$

$$Y_{MD30} = 42.7 + 46.18x_1 - 13.23x_1^2 + 0.21x_2^2 - 1.36x_1x_2 \quad (6)$$

$$Y_{MD50} = 20.95 + 68.18x_1 - 22.77x_1^2 + 0.39x_2^2 \quad (7)$$

$$Y_{MG30} = -135.5x_1 + 6.3x_2 + 50.7x_1^2 + 8.7x_1x_2 \quad (8)$$

$$Y_{MG50} = -96.55x_1 + 6.02x_2 + 35.82x_1^2 + 5.6x_1x_2 \quad (9)$$

The correlation coefficients (R) and p values of the functions representing the degradation percentage for both inocula after 50 days are shown in Table 3. The regression model that was selected is considered to be adequate to describe the data and the relationship between the independent and dependent variables.

Conversely, the correlation coefficients and p values obtained from the rest of the treatment models designed to represent the biodegradation percentage and the biogas production were not favorable (data not shown). It is proposed that the low organic matter content and the presence of the contaminants influenced the biogas production.

However, the values obtained from the statistical analysis of these samples do give a general idea about the process performance when such conditions occur, especially in the case of biogas production/inhibition owing to the presence of PAHs.

3.2. Overall degradation of the contaminants

The anaerobic degradation of the PAHs under the different conditions studied was evaluated after 30 and 50 days incubation to monitor the process.

Fig. 1 shows the results obtained under thermophilic and mesophilic conditions. After 30 days, all samples showed some degradation and the same trend under the two temperature conditions was observed. The biodegradation observed seems to demonstrate that the native microorganisms of the inoculum (thermophilic or mesophilic) have the catabolic capacity to degrade the PAHs used, and it could be an indication that the methanogenic metabolism becomes coupled to the anaerobic degradation of the PAHs, as observed in other studies (Chang et al., 2006; Yuan and Chang, 2007).

Table 1. Characteristics of inocula and soil used in the experiments

Inoculum/parameter	TS (w.b.)	OM (d.b.)	TOC (d.b.)	TKN (d.b.)	pH	EC	Density (g/L)
Thermophilic	11.8	37.7	20.9	2.03	7.8	8.8	1113
Mesophilic	10.02	39.1	32.8	2.5	7.9	29.9	1013
Soil	93.3	3.7	1.26	0.7	6.7	0.2	-

TS: total solids (%); OM: organic matter (%); TOC: total organic carbon (%); TKN: total Kjeldahl nitrogen (%); EC: electrical conductivity (mS/cm); w.b.: wet basis; d.b.: dry basis.

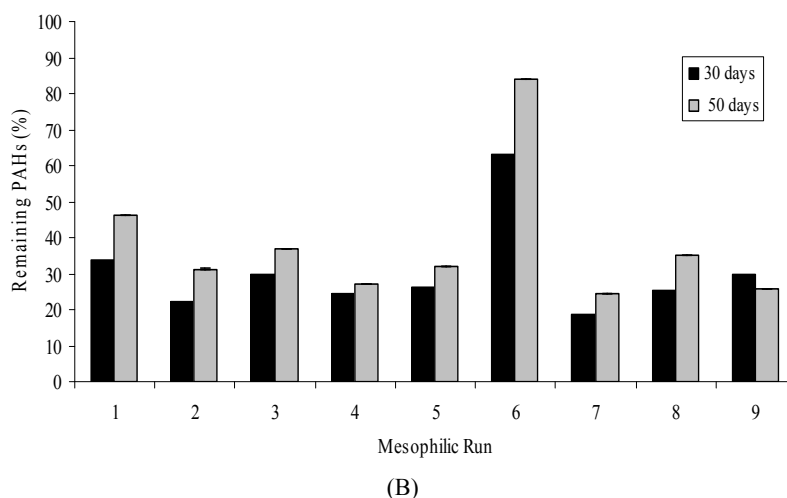
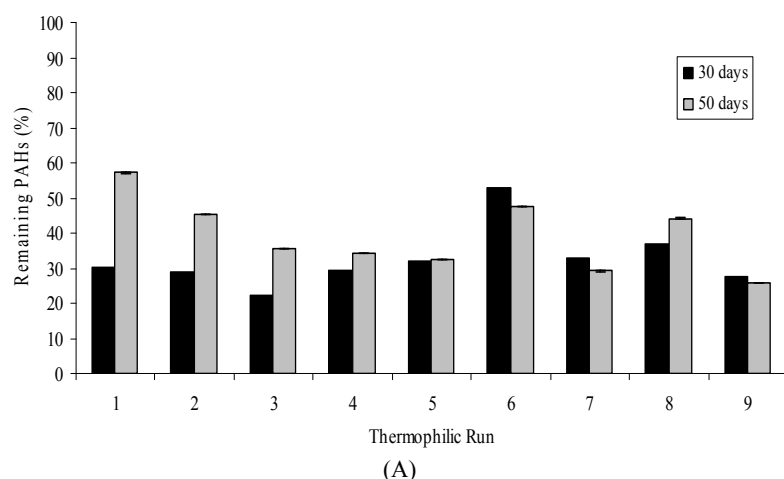
Table 2. Design matrix including factor levels (coded and actual) and the response values for these two factors

Ru n	Factor levels				Y_{TD30}	Y_{TD50}	Y_{MD30}	Y_{MD50}	Y_{TG30}	Y_{TG50}	Y_{MG30}	Y_{MG50}
	Coded		Actual									
	Concen tration (x_1) (g/kg)	Mixing ratio (x_2) (soil:ino culum)	Concentr ation (g/kg)	Mixing ratio (soil: inoculu m)								
1	-1	-1	0.38	0.9:1	69.96	42.89	66.36	53.82	-15.2	-10.9	-20.2	-5.9
2	+1	-1	1.74	0.9:1	71.25	54.78	77.75	68.83	4.8	6.8	-36.4	-27.6
3	-1	+1	0.38	4.3:1	77.58	64.55	70.12	63.12	0.4	1.1	-6.8	-0.9
4	+1	+1	1.74	4.3:1	70.71	65.87	75.43	72.92	4.5	5.3	-6.3	-1.7
5	0	0	1.05	2.6:1	67.91	67.43	73.92	67.90	-3.2	-3.0	-11.4	-5.4
6	$-\alpha$	0	0.1	2.6:1	47.26	52.57	36.8	16.04	-2.1	-3.1	-11.5	-2.1
7	$+\alpha$	0	2.0	2.6:1	67.17	70.83	81.23	75.57	-1.9	3.6	-12.1	-7.7
8	0	$-\alpha$	1.05	0.2:1	62.91	55.82	74.57	65.00	12	23.7	-133.3	-97.0
9	0	$+\alpha$	1.05	5:1	75.59	74.21	70.00	74.17	-1.0	0.4	-3.8	-0.70

*The response represents the degradation (D) percentage (Y_D) and the biogas (G) production (Y_G) after 30 and 50 days of incubation where: T: thermophilic; M: mesophilic and 30 or 50 represents the incubation time (day)

Table 3. Correlation coefficients (R) and p-values of each function (cf. Eqs. 2–9) representing the treatment process

	Thermophilic				Mesophilic			
	Y_{TD30}	Y_{TD50}	Y_{TG30}	Y_{TG50}	Y_{MD30}	Y_{MD50}	Y_{MG30}	Y_{MG50}
R	0.65	0.93	0.65	0.70	0.86	0.89	0.78	0.79
P	0.63	0.06	0.61	0.5	0.17	0.03	0.16	0.15

**Fig. 1.** Percentage (%) of PAHs remaining after 30 and 50 days incubation. (A) Thermophilic conditions and (B) mesophilic conditions

However, the samples containing low concentrations of PAHs (0.1g/kg) resulted in the lowest degradation rate, suggesting that microbial activity is governed by the pollutant concentration in which a minimum threshold level is required to initiate degradation and catabolic induction in biodegrading microorganisms (Boethling and Alexander, 1979).

It is also worth noting that, at low concentrations, more surface area on the soil particles is available for adsorption of the contaminant relative to high concentrations. Therefore, a stronger interaction between the soil and contaminant could be formed making the accessibility and biodegradation of the contaminant complex (Table 4) in which, for the most part, the "F" fraction at low concentrations is lower than at the corresponding high concentrations. In addition, a part of the biodegradation could be related to the soil's endogenous microorganisms because the used soil was not sterilized.

In general, degradation capacities under mesophilic conditions were higher than those obtained under thermophilic conditions. However, thermophilic conditions resulted in better rates of biodegradation when low concentrations of PAHs were used. This phenomenon can be explained by high temperatures, which, in most cases, increase the desorption of PAHs and their solubility, as observed in the determination of the bioavailable portion of the contaminants, relative to the corresponding mesophilic conditions (Table 4). Moreover, under thermophilic temperatures the mass transfer and reaction kinetics are enhanced. Nevertheless, other studies have reported contradictory results. For instance, Chang et al. (2002) found that a temperature of 30°C enhanced PAH degradation better than at 40°C.

Under the different combinations and conditions, and according to the obtained results regarding the contaminants bioavailability (Table 4), the biodegradation of the contaminants was controlled by their characteristics such as water solubility, number of benzene rings and structural conformation (shape) of the molecules. However, no reliable trend or order in biodegradation is apparent.

Analysis of selected components of PLFA demonstrated that anaerobic bacteria were present in all samples, but their abundance in the thermophilic samples was higher than in the mesophilic ones (Table 5). Furthermore, moderate to high PAH concentrations significantly ($p < 0.05$) altered the microbial community structure by changing anaerobic communities in such a way that more anaerobic microorganisms were observed at high PAH concentrations under both conditions, and better degradation rates of PAHs were consequently achieved. The PLFA profiles were in agreement with the rates of PAH degradation (Fig.1) under both conditions with less degradation observed at low PAH concentrations. According to Donald et al.

(1998), the microbial community responded to PAHs contamination at both the phenotypic and genotypic levels, which is also in agreement with the obtained results.

As expected for biological treatments of PAHs, their concentration decreases with time as a result of the microbial activity, or no change occurs in the case of the process failure or absence of optimal conditions for microbial activity. However, in this study the results were completely contradictory to what was expected. For the majority of samples under both conditions (37 and 55°C), it was found that the PAH concentrations after 50 days of incubation were higher than those obtained after 30 days. We therefore propose the following hypotheses: a) sorption or occlusion of the contaminants (PAHs) in the organic matter during the first 30 days and release after depletion of biodegradable organic matter, b) new PAHs bioformed under these conditions. To examine the potential impact of sorption on the results, representative samples (in duplicate) were extracted twice under extreme conditions: high temperature (200°C), pressure (206.84 bar) and 4 static cycles (10 min). The same samples were also extracted by using a Soxhlet and analyzed as explained elsewhere (Sayara et al., 2010). The extraction and analysis methods resulted in values that corroborated an increase in the PAH concentration. Indeed, Thiele et al. (2002) demonstrated that PAHs were formed in soil under oxygen deficient conditions. In that study, the concentration of high molecular weight PAHs (more than 3 aromatic rings) increased considerably, whereas for compounds with three rings the concentration decreased, probably owing to anaerobic biodegradation. Furthermore, the incubation of edible oil in closed containers at room temperature led to the formation of PAHs (Guillen et al., 2008) indicating that anaerobic conditions are likely responsible for such a phenomenon.

3.3. Metabolites

The observed initial decreases in the concentration of PAHs show that the inocula were able to degrade the target contaminants. Anaerobic biodegradation of PAHs was also monitored by analyzing the metabolites produced as a result of microbial activity in the samples (Table 5). In fact, several compounds were identified by GC-MS. These compounds included: phenol, hydroxyfluorene, benzenecetic acid, cresol, pyridine, fluorenone, fluorenol, carbazole, anthracenone, anthracenedione, biphenyl and anthrone. These compounds are known metabolites generated when PAHs are degraded by microorganisms through several oxidation pathways. Consequently, the metabolites found in this study provide evidence of the microbial capacity to degrade PAHs under the conditions studied. PAH degradation pathways under anaerobic conditions are still not clear, and various hypothesis or arguments

are found in the literature. Meckenstock et al. (2004) and Zhang and Young (1997) argued that carboxylation is the initial step in PAH biotransformation under sulphate reducing conditions. On the contrary, Bedessem et al. (1997) proposed hydroxylation as the initial step in PAH biotransformation under the same conditions. Vogel and Grbic-Galic (1986) argued that the anaerobic transformation of benzene and toluene to CO_2 and CH_4 occurred through hydroxylation, when phenol and cresol were identified as intermediates of benzene and toluene, respectively.

Because these compounds have been identified in the present study, it would be possible to assume that hydroxylation was the initial step occurring during the biotransformation of PAHs in this case. Most likely, PAHs undergo initial ring reduction followed by hydrolytic ring cleavage to yield aliphatic acids for cell growth. Moreover, naphthalenol was detected as metabolite from naphthalene biotransformation in sulfidogenic sediments (Bedessem et al., 1997). All of these observations support the hypothesis that PAHs degrade under methanogenic conditions and hydroxylation is the initial step in their biotransformation. Unfortunately, there are no studies that investigate PAH biodegradation under anaerobic conditions, at thermophilic temperatures.

3.4. Biogas production

The cumulative biogas production under thermophilic and mesophilic conditions is shown in Fig. 2. It is clear that the methanogenic inocula under both temperature conditions were exposed to inhibition effects because the PAHs were detrimental for the microorganisms. Usually, under similar conditions, an adapted ecosystem is used to avoid this inhibition.

Consequently, as shown in Fig 2, an adaptation period of at least 20 days was needed in most cases except for Runs 2 and 8 under thermophilic conditions. The inhibition rate (negative values indicate that biogas production in the control samples is higher than in the samples containing PAHs) gradually increased with time indicating an increase in toxicity of the samples.

However, in most samples, after 20 days' incubation, biogas production changed and inhibition decreased over time, although not completely eliminated in the mesophilic samples. In addition, process recovery was noted with prolonged incubation times and methane production was observed and increased significantly following the inhibition stage (data not shown). This observation demonstrates that both of the inocula were not previously exposed to similar contaminants and agree with the preliminary analysis that showed that they were free from PAHs. Interestingly, the study clearly indicated that although the presence of PAHs considerably inhibits biogas production, PAH degradation is not affected.

Indeed, Fuchedzhieva et al. (2008) reported similar behavior for fluoranthene biodegradation, which continued despite cell growth inhibition in the presence of a biosurfactant complex. In general, better results were obtained for the samples treated under thermophilic conditions relative to mesophilic ones, because the higher temperatures facilitate the reaction rates and enhance enzymatic activity. However, microbial activity can be hampered by the presence of toxic metabolites resulting from degradation of the parent compounds. Indeed, analysis showed high rates of toxicity in all samples relative to a non-toxic control (data not shown). This toxicity is likely owing to the PAHs themselves and their metabolites as a result of microbial biodegradation.

Additionally, the ratios of saturated to monounsaturated PLFAs (S/M) and the ratios of cyclopropyl PLFAs to their monoenoic precursors (cy/pre) (Table 5) were significantly higher in the mesophilic samples relative to the thermophilic ones, indicating microbial community stress under such conditions (Moore-Kucera and Dick, 2008).

However, analysis of volatile fatty acids showed that there is no inhibition caused by such acids because they were not detected in any sample after 30 or 50 days. The pH values of the sample mixtures after 30 and 50 days were within 7.3–7.9, which is around the optimal values for anaerobic digestion. Therefore, the fluctuation of biogas production observed was more likely owing to some PAH metabolites that were formed transiently during their anaerobic biodegradation. The oscillation in the biogas production (Fig. 1, thermophilic run 8) clearly shows this effect.

3.5. Process response for PAH degradation

The variations in PAH degradation (%) under the conditions studied factors are shown in Fig. 3 and Fig. 4 for thermophilic and mesophilic inoculum, respectively. Under mesophilic conditions, it is clear that the degradation capacity is always proportional to PAH concentration, whereas the soil to inocula mixing ratio was found to influence PAH degradation at low concentrations (less than 1 g/kg). For instance, low (0.2:1) or high (5:1) mixing ratios enhanced the degradation rate, but intermediate ratios negatively affected the process.

The same behavior was observed under thermophilic conditions during the first 30 days, although PAH concentration influenced the degradation capacities to a smaller extent (Fig. 3A). Nevertheless, after 50 days the degradation capacity response demonstrated that the process is proportional to both factors, with the highest degradation (75%) being obtained at the highest concentration and mixing ratio. The increased toxic potential of higher PAH concentrations on the inocula can explain why degradation decreases as inoculum ratio increases. Similar results were seen

with the increase of the inoculum ratio under anaerobic conditions (Chang et al., 2002).

In both cases the PAH degradation was clearly proportional to the soil to inocula mixing ratio and the best results were obtained when using the highest ratio (5:1). These results are in accordance with those obtained by Hernandez et al. (2008) who reported that increasing the concentration of substituted phenolic compounds enhanced the anaerobic digestion process, but that at higher concentration the total biodegradation decreased. The sequential decrease in biogas production (Fig. 2) observed during the first three weeks demonstrates the difficulties the microflora had to overcome to adapt their biodegradation potential. Here, time was an essential factor to allow for effective microbial adaptation under these conditions.

Although PAHs and their metabolites had an inhibitory effect on the methanogenic communities, other anaerobic microbes were able to continue the degradation process. Interestingly, PAH degradation increased when a high soil to inocula ratio was used for both cases. This observation is fundamental when considering an economical evaluation because larger quantities of contaminated soil could be treated with smaller quantities of inoculum. Because no other nutrient sources were available to the microorganisms, it is likely that the organic matter of the soil served as the nutrient source, and that, because the organic matter content was low, this nutrient limitation motivated the microorganisms to use PAHs. However, the addition of an organic matter source, such as compost, could stimulate microbial activity and, consequently, accelerate PAH degradation. This effect was clearly demonstrated in previous studies (Darush et al., 2006; Sayara et al., 2010).

3.6. Process response for biogas production

The response of biogas production under thermophilic and mesophilic conditions is shown in Fig. 5. The value for the biogas produced by a sample was calculated by subtracting the value obtained from the control experiment (only inoculum present) from the value obtained from the contaminated soil sample. The negative values indicate that the background biogas production was higher than for the contaminated samples owing to inhibition. The process behavior was completely different under thermophilic and mesophilic conditions, with no biogas being produced under

mesophilic conditions, whereas certain amounts were produced under thermophilic conditions in several samples. A soil to inoculum mixing ratio of almost 3:1 was the inflection point in relation to the applied concentrations (0.1–2 g/kg). A soil to inocula ratio higher than 3:1 was gently influenced by the variation in PAH concentration.

The biogas production rate slightly increased with increasing PAH concentration under thermophilic conditions, whereas no variation was seen with mesophilic inocula (stagnation state). At mixing ratios below 3:1, different behaviors were observed demonstrating various interactions between the studied variables within the two temperatures domains. Up to a point (almost 1.4g /kg), increasing the concentration of PAHs enhanced the biogas production rate under thermophilic conditions. Thereafter, further increases in PAH concentration negatively affected the microbial activity because of their toxic properties.

Moreover, biogas production was enhanced at low soil to inoculum ratios when additional inoculum was introduced. Nevertheless, increasing inoculum quantity negatively affected the biogas production under low PAH conditions (<0.2g/kg). Under mesophilic conditions, the rate of inhibition gradually decreased as the soil to inocula ratio increased until a ratio of 3:1 was achieved. Above this ratio, the rate of inhibition plateaued. PAH concentrations below plateau conditions (mixing ratio less than 3:1) influenced the process in two different ways: an increase in PAH concentration was followed by an increase in the inhibition rate until a certain concentration was reached (almost 1g/kg) after which the process changed its behavior and a decrease in inhibition was observed.

4. Conclusions

A comparative study on the anaerobic bioremediation of PAH-contaminated soil under methanogenic conditions, at thermophilic and mesophilic temperatures, has been conducted.

This study indicates that inhibition of biogas production is related to high concentrations of PAHs. Although a high rate of biodegradation was achieved during 30 days, a prolonged incubation time for both thermophilic and mesophilic samples showed an increase in the PAH concentration. This increase was probably caused by the reverse bioformation of these compounds.

Table 4. Values of “F” fraction (%) for each component after 50 days for samples 5, 6 and 7 under thermophilic (T) and mesophilic (M) conditions

	<i>T-5</i>	<i>T-6</i>	<i>T-7</i>	<i>M-5</i>	<i>M-6</i>	<i>M-7</i>
Fluorene	96.0	100.0	97.15	88.94	100.0	77.75
Phenanthrene	89.1	100.0	98.65	74.15	98.38	79.08
Anthracene	69.7	77.09	81.38	70.89	93.33	73.58
Fluoranthene	83.24	70.68	94.81	86.45	91.98	90.25
Pyrene	68.17	ND	92.94	70.23	4.31	78.75

ND: not detected (below the detection level)

Table 5. PLFA structure of the microbial biomass for samples 5, 6 and 7 after 30 and 50 days under thermophilic (T) and mesophilic (M) conditions

<i>Biomass/Treatment</i>	<i>T-5-30</i>	<i>T-6-30</i>	<i>T-7-30</i>	<i>M-5-30</i>	<i>M-6-30</i>	<i>M-7-30</i>	<i>T-5-50</i>	<i>T-6-50</i>	<i>T-7-50</i>	<i>M-5-50</i>	<i>M-6-50</i>	<i>M-7-50</i>
Fungi	2376.38	404.45	1031.77	1139.98	894.5	1256.78	1233.92	1034.08	1664.3	814.67	1139.79	804.89
Bacteria	83862.03	1399.42	2241.85	10670	11112.8	11264.8	2751.07	3575.27	3818.31	13201.8	13485.3	10294.2
Actinobacteria	455.42	134.46	272.89	665.29	632.97	669.43	290.03	380.47	329.7	544.23	712.66	600.43
Gram positive	2521.82	916.95	1153.36	8035.5	8616.16	8570.36	1625.29	2253.64	2357.06	10825.8	10476.3	8111.61
Gram negative	1202.15	283.71	736.54	1768.22	1648.93	1822.75	701.02	760.37	974.36	1591.95	2021.35	1396.72
Anaerobic bacteria	145317.6	24332	77354.3	42321.8	35682.2	44730.5	80674.3	83980.6	91905.5	34616.1	46113	33856.2
Total microbial biomass	163930.3	29044.1	87662.3	60262.1	53775.3	63563.4	91591	97311.7	105652.4	55498.7	67997.1	50700.7
Sum (cy17:0, cy19:0)=Cy	145.02	59.26	116.15	475.91	439.12	485.66	106.21	136.97	111.12	422.25	525.2	349.95
Sum(16:1w7,18:1w7)=Pre	1028.51	214.61	605.59	1250.36	1168.43	1287.89	580.19	602.89	843.19	1130.94	1456.3	1012.51
Ratio (Cy/Pre)	0.15	0.27	0.2	0.38	0.38	0.38	0.18	0.23	0.13	0.37	0.36	0.34
Saturated PLFA (S)	12191.59	3029.16	7229.61	6782.45	6712.44	6976.2	7163.7	9020.58	8519.43	7499.67	8024.28	6256.48
Monosaturated PLFA (M)	146229.7	24497.2	77858.5	43138.2	36452.9	45581.9	81162.9	84467	92657.62	35363.5	47084	34553
S/M	0.08	0.12	0.1	0.16	0.19	0.15	0.09	0.11	0.09	0.21	0.17	0.18
Anaerobic bacteria/total biomass	0.89	0.84	0.88	0.7	0.66	0.7	0.88	0.86	0.87	0.62	0.68	0.67

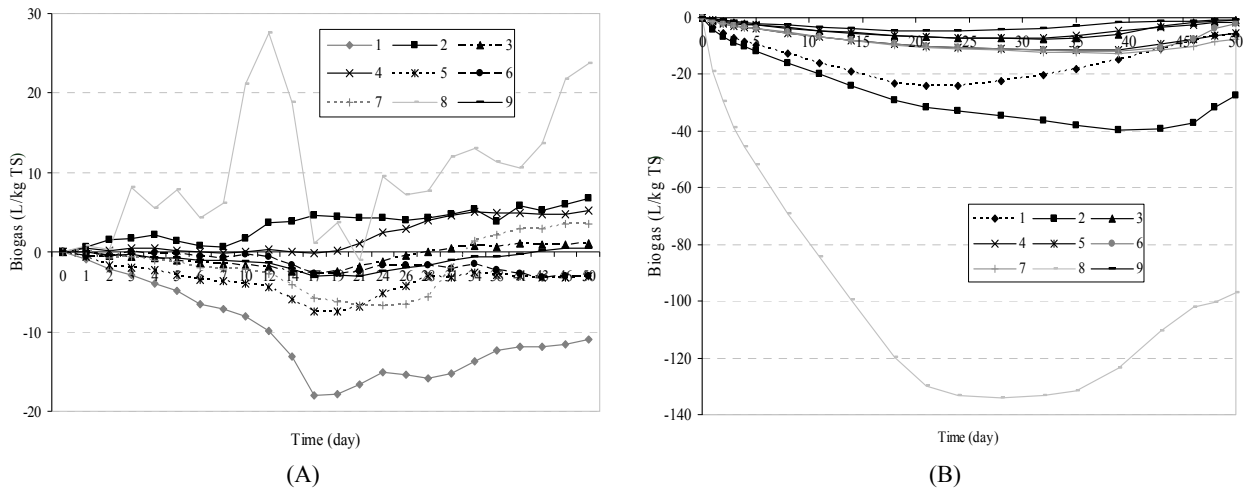


Fig. 2. The cumulative biogas production (L/kg TS) after 50 days. (A) Thermophilic conditions and (B) mesophilic conditions

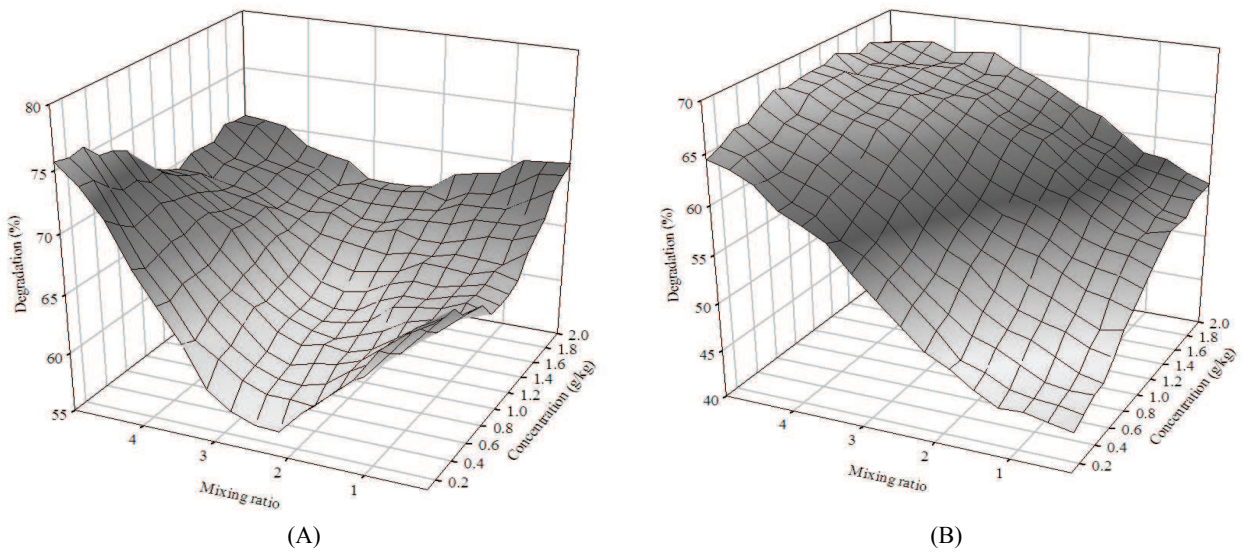


Fig. 3. Response of PAHs degradation (%) under thermophilic conditions. (A) After 30 days and (B) after 50 days

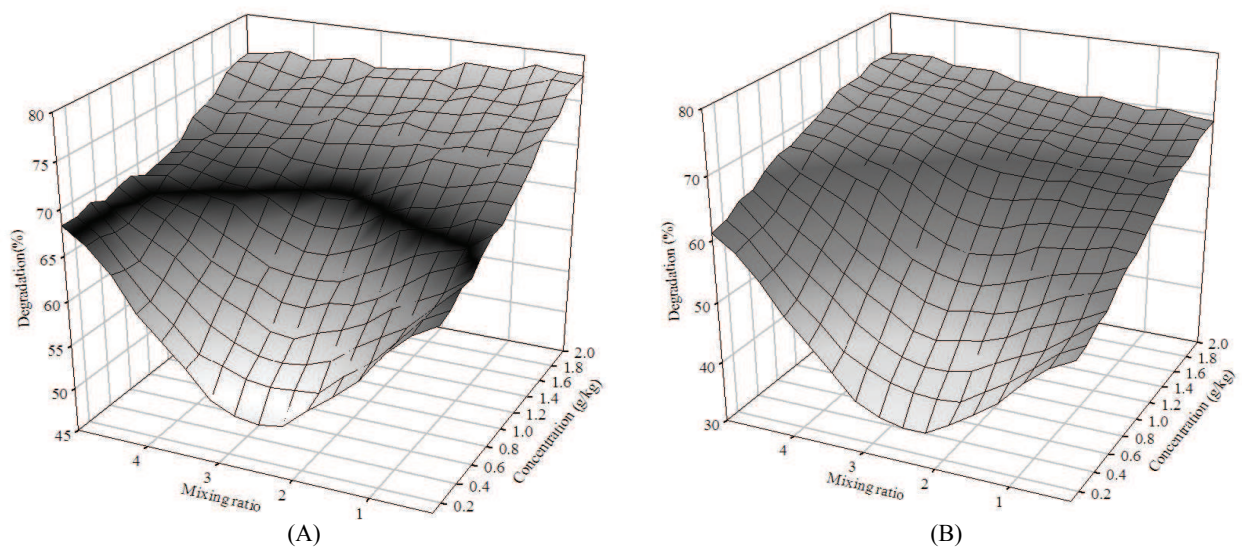


Fig. 4. Response of PAHs degradation (%) under mesophilic conditions. (A) After 30 days and (B) after 50 days

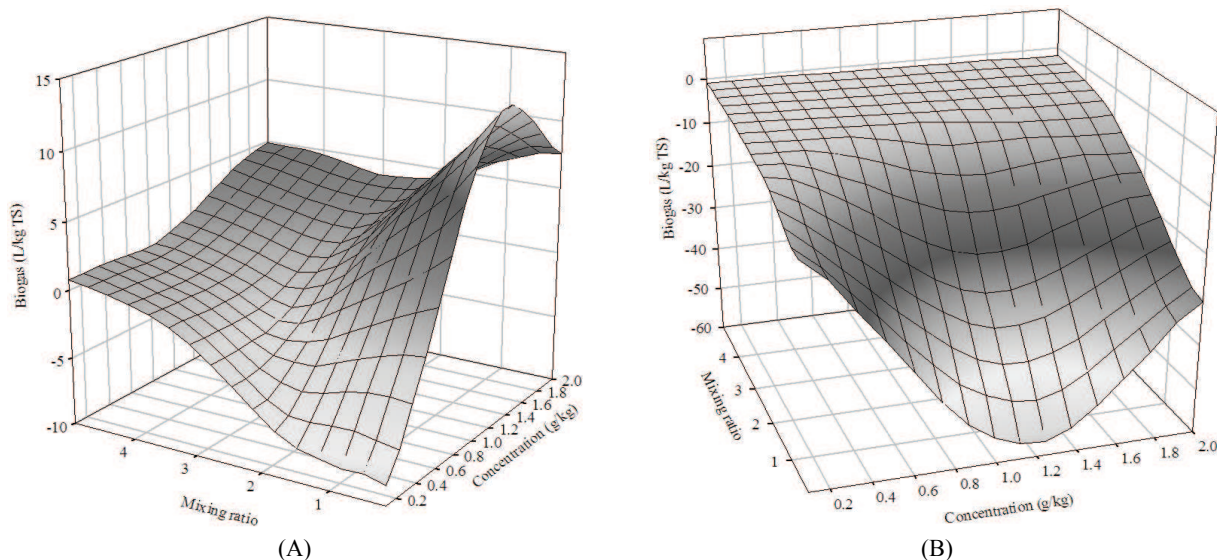


Fig. 5. Response of the total biogas production (L/kg TS) after 50 days. (A) Thermophilic conditions and (B) mesophilic conditions

Further research is necessary to clarify this effect and to determine exactly the optimal times required for biodegradation.

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PRODUCT ECODESIGN IN COMPANIES WITH ISO 14001 CERTIFIED ENVIRONMENTAL MANAGEMENT SYSTEM

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Abstract

Product eco-innovation based on ecodesign principles is based on the idea of including the environmental aspects of a product over its entire life-cycle, thus providing the opportunity for manufacturing companies to intervene earlier during product development processes. The aim of this study was to gather information and evaluate the situation regarding ecodesign within the ISO 14001 certified medium and large manufacturing companies in the Republic of Slovenia by means of a questionnaire. The goal was to identify the most important environmental criteria taken into account during product development and to reveal whether ecodesign measures as a result of adopting ISO 14001 certification being promoted or not. The results revealed that companies channeled most of their product-development attention towards waste and energy reduction during manufacturing processes, reduction of material consumption per unit of product, reducing air and water emissions, as well as the replacement of toxic and hazardous substances. The importance of different ecodesign criteria 'reduction of material consumption per unit of product' was reported as the most important criterion for Slovene ISO 14001 certified manufacturing companies. Most of the analyzed firms considered the ISO 14001 standard to be a very useful tool, or at least a useful tool, for helping them to accelerate and establish product ecodesign activities.

Key words: ecodesign, environmental management system, ISO 14001, products

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1. Introduction

It is clear, that if the environmental impact from industry is to be reduced, it is insufficient to only regulate emissions from manufacturing processes alone. Therefore, the focus is changing from processes to products, as environmentally improved products are becoming increasingly vital for business success. Numerous authors have commented on the importance of product development for improving a firm's environmental performance (e.g. Brezet and van Hemel, 1997; Fiksel, 1996; Hanssen, 1999; Reijnders, 1996; Tischner and Charter, 2001). However, product eco-innovation is a relatively young discipline. In 2000–

2002, only 14 percent of innovative companies within the EU-27 declared that "reduced environmental impacts or improved health and safety" had highly-important effects on their innovation activities (Reid and Miedzinski, 2008). A study of European small and medium-sized enterprises found that 25 percent of companies had introduced a new or significantly improved eco-innovative product onto the market (Survey EC, 2011). Nevertheless, the situation is now changing rapidly. Legislation relating to the environmental impact of products is being implemented at an increasing rate worldwide. Moreover, the European Commission is currently working on the development of a harmonized methodology for the

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calculation of so-called environmental footprints of products, with the aim of reducing further their environmental impacts. Within this policy the emphasis will be given to life-cycle environmental impacts and the least environmentally-friendly products are planned to be cut-out from the market (Galatola, 2011). Therefore, many companies have started to systematically improve their environmental performances regarding their products.

Environmental impacts occur during all stages of a product's life cycle, including raw material extraction, production, sales, distribution, transport, usage, maintenance, and waste treatment. These impacts may be either short-term or long-term, and they may occur at local, regional, and/or global levels. In addition, different types of products impact differently during the stages of their life cycles. These impacts can be reduced or even eliminated through design and development decisions.

The ecodesign of products is defined as "the integration of environmental aspects into product design and development, with the aim of reducing adverse environmental impacts throughout a product's life cycle" (ISO, 2010a). Therefore, the central aims of ecodesign are to reduce the consumption of primary resources, optimize production and distribution, prolong the lifespan of the product, use fewer hazardous materials, increase the use of recycled materials, and/or make waste treatment easier and more efficient both environmentally and economically. Since most of the environmental burdens of a product are determined at the design stage, this stage is the crucial step when improving a product's environmental performance. Therefore, the principle of ecodesign is based on a preventive approach: if environmental considerations are taken into account during the earliest phases of product development, then it is more likely that the product's overall environmental impact can be significantly lowered.

An increasing number of enterprises around the world have accepted the ISO 14001 as the standard by which they certify their environmental management systems (EMS). EMS according to ISO 14001 has been a trend within Slovenian manufacturing and service companies since 1997, and for many of them it has also become a precondition for entering foreign markets (Radonjič and Tominc, 2006, 2007). In Slovenia, 12 companies were certified in 1998 (a year after the adoption of ISO 14001 as a Slovenian national standard), and this number had risen up to 284 companies by 2005. In 2009 the number of certified companies had reached 390. Slovenia now ranks highly amongst EU countries, based on the number of certificates per capita-base: in 2009 the number was 191 ISO 14001 certifications per million citizens whereas the EU-27 average was 162 certificates (ISO, 2010b). Slovenia also ranks highly when comparing a ratio of ISO 14001 certifications to national GDP (expressed in milliard EUR): in 2009 this ratio was 6.8 for the EU-27 average and 11.4 for Slovenia (Eurostat, 2011).

The ISO 14001 standard provides an internationally-recognized framework for environmental management, measures, evaluation, and auditing. From amongst other requirements, ISO 14001 necessitates an organization for establishing an appropriate environmental policy; identifying those environmental effects resulting from the organization's past, present or future activities, products, and services; identifying priorities; setting appropriate environmental objectives and targets; and facilitating planning, control, monitoring, preventive, and corrective actions in order to minimize any impact on the environment. Decisions to adopt EMS and develop effective implementation strategies according to ISO 14001 requirements may lead to many benefits for companies, including considerable potential for improving various environmental indicators, as reported by Ammenberg and Hjelm (2002); Hillary (2000); Morrow and Rondinelli (2002); Nishitani, (2009); Radonjič and Tominc (2006, 2007); Raines (2002); Zutshi and Sohal (2004). This paper is structured as follows: Chapter 2 reviews the theoretical and empirical literature on the incorporation of eco-design and product development practices within ISO 14001 implementation in different countries, in order to formulate the aim and goal of this research. Chapter 3 describes the objective of this research, whilst Chapter 4 presents the applied research strategy and methodology. Chapter 5 presents the empirical results together with explanation and discussion on the main findings. This paper concludes with the main conclusions and suggests certain directions for future research.

2. Theoretical background: Incorporation of ecodesign and product-development practices within an ISO 14001 environmental management system

When effectively applied, an EMS can help integrate environmental considerations within an organization's overall management system. Findings have been reported that EMS implementation, according to the ISO 14001 requirements, has more or less positively influenced the environmental performance of industrial companies within different countries and in various industrial sectors (Ammenberg and Hjelm, 2002; Andrews et al., 2003; Berkhout et al., 2004; Dahlström et al. 2003; Gomez and Rodriguez, 2011; Hertin, 2004; Hillary, 2000; Morrow and Rondinelli, 2002; Nishitani, 2009; Radonjič and Tominc, 2006, 2007; Raines, 2002; Schylander and Martinuzzi, 2007; Wehrmeyer et al., 2002; Zutshi and Sohal, 2004).

Although the products are key linking elements between their producers and the natural environment, other business environments and homes it seems that they are still not widely regarded as significant environmental factors within the main scope of EMS policies, where the sites and processes tend to be the focus of optimization. As several researchers have confirmed, the benefits of ISO

ISO 14001 implementation for companies are related, in large part, to process optimization and to related innovations (energy and materials' usage, waste reduction, water consumption, improved workplace safety) that are connected with the reduction of operational costs (Dyllick and Hamschmidt, 2000; Hertin et al., 2004; Radonjić and Tominc, 2006, 2007; Rennings et al., 2006; Schylander and Martinuzzi, 2007; Zutshi and Sohal, 2004; Wagner, 2008). That scope of environmental management that considers impacts outside the factory gate (e.g., the product's use phase and/or waste treatment) in ISO 14001 certified enterprises is often neglected, meaning that the link between EMS and product development in some companies is weak or even completely missing (Ammenbergh and Sundin, 2005b; Johnstone and Labonne, 2009; Kautto, 2006; Morrow and Rondinelli, 2002; Schylander and Martinuzzi, 2007; Wehrmeyer et al., 2002).

What is the reason of this? The extent of an EMS contribution to environmental optimization and the innovation of the processes and products depends on the company's strategic choices. The ISO 14001 standard, on the one hand, mentions products and product design as an issue within the scope of organizations' environmental management activities that can be influenced by using proper measures. On the other hand, it states that organizations do not have to consider each product but rather select product categories, by taking into account the inputs and outputs (both intended and unintended) associated with these products. However, the standard suggests that identifying the environmental aspects of a product does not require a detailed life cycle approach, which is, however, at the core of the ecodesign concept (ISO, 2004).

Although product development is not the primary focus of ISO 14001, the standard can provide guidance for the establishment of EMS, that can be broadened in connection with product design and development. An EMS is flexible enough to promote environmental policy more broadly, including not only on-site pollution prevention measures but more efficient use of all inputs. With respect to this, an organization can establish a methodology based mainly on environmental criteria, which should take into account as many environmental impact categories as possible, including products (ISO, 2004). Ecodesign, on the other hand, discusses the incorporation of environmental aspects into the design and development activities of products from the point of view of which is broader. This is because it should be based, by definition, on the entire product life cycle (including those phases which are not within the direct control of the company). Product ecodesign could, therefore, strengthen a company's overall proactive environmental policy efforts regarding life cycle thinking. However, in order to carry out ecodesign in a systematic and manageable way, organizations need to implement appropriate activities with necessary levels of competence in

order to effectively carry out and manage these activities. This needs the support of top management, who are also responsible for EMS implementation. Of course, both approaches can be developed separately. However, they are mutually related in the sense that both concepts try to reach the goal of reducing negative environmental impacts, even though their concepts differ. Therefore, synergistic effects can be obtained if ecodesign is properly included within an already established proactive environmental policy. Like any other methodology or engineering tool, ecodesign needs the support of firm's management, in order to be accepted in practice.

In order to broaden the potential of EMS, the International Standardization Organization published a standard ISO 14006 entitled "Environmental management system – Guidelines for incorporating ecodesign" (ISO, 2010), which should provide guidelines that assist organizations in establishing, documenting, implementing, maintaining, and continually improving their management of ecodesign, as part of an EMS. As standard ISO 14006 points out, those general areas of knowledge required to carry out ecodesign within an EMS include an assessment of the products' environmental impacts, identification of appropriate design measures to reduce these impacts, and management of the product design including the implementation of design measures (ISO, 2010). This means, that if ecodesign is to be successful, it must be incorporated within a management system (Brezet and Rocha, 2001; Fiksel, 1996; Reijnders, 1996). Since the research and development activities within certain manufacturing company is led by the top management, it is clear that shift from old to improved products must be a part of the decision process by responsibly taking into account as many environmental protection requirements as possible. Without the inclusion of product design within an overall environmental policy serious gaps can occur that diminish a company's impact on the environment. For example, Johansson, (2002) and Boks, (2006) summarized the results of several studies regarding success factors for integration of ecodesign into product development, and showed that the success of such integration is largely dependent on management commitment and support when clear environmental goals need to be established. Therefore, it can be expected that environmental burdens from products' life cycles would be reduced if product development is strengthened within an already existing EMS.

Regardless of intensified environmental product development worldwide as a consequence of market and regulatory pressures, there are still few in-depth studies available that deal the topic of product ecodesign in relation to EMS adoption. Frei, (1998) reported that although ISO 14001 certified companies give higher significance to sustainable product design compared to non-certified ones, there is a weak point of translating environmental aspects

into product design showing a certain gap between environmental management and product design. That was further confirmed by Ammenberg and Sundin (2005b) regarding Swedish companies. They showed that EMS auditors seldom pay attention to product characteristics such as resource demands during the use phase, impacts during the end-of-life phase, recyclability, etc. Grüner et al. (1999) studied German companies using EMS in their practice and their findings were that either none or only a very weak link was observed between EMS and product development. Similar trends were reported by Kautto (2006) for the Finnish electrical and electronic industry, and Schylander and Martinuzzi (2007) for Austrian companies.

Despite these discouraging reports, some researchers have reported more successful practices that link product development and/or ecodesign measures within ISO 14001 EMS. Special product-oriented EMS projects have been developed in the Netherlands with the aim of embedding ecodesign within firms on a continuous basis, rather than on an individual project basis (van Berkel et al., 1999; Brezet and Rocha, 2001; Ammenberg and Sundin, 2005a; 2005b). Product-oriented EMS is considered to be a logical extension of the already-existing and wider-implemented EMS that is mainly process- or facility oriented. Van Berkel et al. (1999) summarized the successful ecodesign projects of Dutch retail and industrial companies that cooperated in a project that resulted in environmental improvements to their products. In addition, the studies of Rehfeld et al. (2007) and Ziegler and Rennings (2004) showed that certification of EMS based on ISO 14001 can have a positive effect on overall environmental product innovations. Some authors further confirmed the link between EMS and product development. However, they showed that such a link is still more often associated with process innovations and to a lesser extent with product innovations (Hertin et al., 2004; Rennings et al., 2006; Wagner, 2007; 2008; Ziegler and Seijas Nogareda, 2009). It has to be emphasized that the terms eco-innovation and ecodesign are not synonyms, although they are connected to a certain point. Namely, ecodesign means a specific concept using life-cycle methodology and tools within broader product research and development process at different levels, which can lead to innovative products. Therefore ecodesign, as a methodological approach, opens up additional possibilities for product eco-innovations.

It is clear from literature review that empirical information on the relationship between ISO 14001 EMS and product ecodesign practices remains limited, and even contradictory. Previous studies have not provided clear answers to the question as to what effect does EMS appear to have on product ecodesign. Not only due to the fact that ecodesign and EMS were developed separately, but also because ecodesign based on a life-cycle methodology is a relatively young discipline that is still widely

unrecognized in practice. Empirical data on such topics are still limited and sparse for different countries and industrial sectors. In addition, certain of the above-mentioned studies were published before various regulatory schemes and directives relating to the environmental aspects of products were implemented within the EU. This, of course, has certain effects on firms' perceptions concerning environmental protection priorities. Various problems regarding product ecodesign and EMS adoption, therefore, remain thus providing a basis for defining the aim and objective of this research.

3. Objective of the study

The literature survey, described in the previous chapter, suggests that studies regarding product ecodesign integration as a part of ISO 14001 EMS remains more or less in its early stages. Although an increasing number of studies have been published on ecodesign, information on how EMS promotes ecodesign activities in different manufacturing sectors is still lacking, especially for those developing countries that joined the EU community later. Furthermore, studies published by other authors mainly deal with the general aspects of ecodesign or product design, with little attention paid to investigating the different ecodesign criteria and priorities in relation to EMS. The presented research framework is based on the idea that product ecodesign is an activity within a firm's internal environmental policy established in-line with the requirements of ISO 14001 certification. A possible link between ecodesign and EMS is supported by the fact that both approaches relate to the defining and choosing of several different environmental impacts, as evaluated by a company. Therefore, mutual relation between two approaches is expressed through their environmental concerns. Ecodesign can be seen as an extension of an EMS program. On the other hand, EMS can serve as a framework (not a driver in the usual meaning of the word) for supporting ecodesign with proper management activities, environmental data, finance, marketing etc.

This paper addresses two aspects concerning product ecodesign. Firstly, desire to identify the most important environmental criteria (indicators) taken into account during product development within companies, to reveal to what extent these criteria are integrated into the product development process (on-site criteria versus impacts outside the factory gate), and to discover what priorities these criteria are given in ISO 14001 certified Slovenian medium and large manufacturing companies. Such findings can reveal an important outcome: do companies put more effort into on-site criteria which are easier to control, or do they also spread their ecodesign efforts with the inclusion of criteria relating to other phases of the product's life cycle. In addition, comparative analyses amongst three selected industrial sectors were carried out in order to reveal the main focuses and preferences for ecodesign of their products. Such

topics have not been widely studied in the context of EMS certification and any related information is still sparse in the literature. Secondly, the aim was to investigate whether the development of environmentally-friendly products is supported by the EMS's adopted by Slovenian manufacturing companies, or not. None of the previous studies have investigated the link between ecodesign and EMS, on such a manner. In order to reach the objectives of the study, the main hypotheses were defined, as follows: Hypothesis 1: Industrial sectors differ with respect to the importance of environmental criteria for ecodesign of their products; Hypothesis 2: An EMS certified according to the ISO 14001 standard affects product ecodesign efforts; Hypothesis 3: The period of the ISO 14001 adoption plays an intense role during ecodesign criteria incorporation.

4. Research methodology

4.1. Description of the sample

This research was based on a questionnaire survey fielded during January and April 2010 to a sample of ISO 14001-certified manufacturing companies that operate within the Republic of Slovenia. The case-studied companies were chosen using the enterprise register of the Slovenian National Chamber of Commerce. Only medium and large enterprises were included, mainly because of two reasons: firstly, from the economic point of view, the contribution of large and medium-sized enterprises to export, as well as to the gross domestic product is significantly higher compared to the contribution of small businesses; secondly, from the organizational, as well as managerial point of view, it is more likely that large and medium-sized enterprises have already established a special department for product development, than have small firms. Although small enterprises represent an important share of environmental impacts because of their greater number, they often face different barriers in the implementation of environmental policies than larger companies do (Hillary, 2004).

In January 2010, the questionnaires were sent directly to the person in charge of each company's product research, design, and/or development activities. In March 2010 telephone calls were made to non-respondents to encourage the persons in charge of product development to fill in the survey. As can be seen in Table 1 a total of 108 questionnaires were sent out, and 61 were returned. Amongst these, five questionnaires were rejected because of missing responses to some of the variables, giving a final response rate of 51.8 percent. More precisely, 46.3 percent of the large and almost 61 percent of medium-sized certified manufacturing companies responded to our questionnaire. Of the firms sampled, 55.4 percent were medium-sized firms and 44.6 percent were large firms¹ (¹ - Enterprises with 50-249 employees are considered

medium-sized and those with 250 employees or more are considered large enterprises).

The firms' main activity, based on NACE Rev.2 Statistical classification of economic activities within the European Community was taken into consideration, as presented in Table 2.

Table 1. Composition of the sample

<i>Company size</i>	<i>Number of all certified companies</i>	<i>Number of all certified manufacturing companies</i>	<i>Number of companies included in the final sample</i>
Large	171	67	31
Medium-sized	93	41	25
Small and micro	125	-	-
Total	389	108	56

Table 2. Structure of the sample by industrial branch

<i>Industrial branch</i>	<i>NACE code</i>	<i>Frequency</i>	<i>Percentage</i>
Manufacture of textiles	C 13	2	3.6
Manufacture of wood and wood products	C 16	2	3.6
Manufacture of paper and paper products	C 17	4	7.1
Manufacture of chemicals and chemical products	C 20	9	16.1
Manufacture of rubber and plastic products	C 22	6	10.7
Manufacture of other non-metallic mineral products	C 23	2	3.6
Manufacture of basic metals	C 25	8	14.3
Manufacture of computer, electronic, and optical products	C 26	2	3.6
Manufacture of electrical equipment	C 27	11	19.6
Manufacture of machinery and equipment n.e.c.	C 28	2	3.6
Manufacture of motor vehicles and trailers	C 29	3	5.4
Manufacture of furniture	C 31	2	3.6
Other manufacturing	C 32	3	5.4
Total		56	100.0

Seventy-three percent of the responding enterprises were domestically-owned, and 26.8 percent were foreign-owned, whilst 92.7 percent of the enterprises in the sample operated predominantly

or mostly in foreign markets, and 7.3 percent operated predominantly within the domestic market. Eighty-nine percent of the companies within the study had their own research and development departments.

In order to improve our insight into the specifics of certain industrial branches, the three with the highest response rates were analyzed in greater detail: the chemical and related industries, the metal industry, and manufacturers of electrical equipment and household appliances. Together these industries represented 50 % of the respondents. The chemical and related industries included branches like the production of chemicals and chemical products, the production of rubber and plastic products, and the production of pulp and paper products. They were grouped into one category since the production of paper is based on the chemical processes of pulp production and the use of chemical agents. The production of plastic products includes plastic processing (but not the production of polymers, which is normally classified within the chemical industry sector) because plastics' manufacturing represents a final step in the manufacturing of synthetic polymers. Many different chemical agents are added to polymers during compounding, and chemical reactions occur in some processes, such as in the production of polymeric foams and thermoset resins. Respondents from the metal industry included enterprises that produce steel and primary aluminum, those that fabricate steel and aluminum, and metal processing manufacturers.

4.2. Environmental (ecodesign) criteria selection

The following procedure was carried out, in order to analyze which environmental criteria (indicators) were taken into account in firms' approaches to ecodesign. When firms reported on more than one product to be developed, the average values for all the reported products were calculated. Based on these averages, cumulative values were determined for the manufacturing sector as a whole, and for the three selected branches. Brezet and van Hemel's UNEP manual was used as a worldwide reference for establishing the environmental criteria in a product's life cycle, which represent the main variables regarding ecodesign practice (Brezet and van Hemel, 1997). Certain limitation regarding ecodesign criteria selection can be addressed to products use phase. Namely, only one criterion (among 15) describes environmental impacts in this particular life cycle phase. The reason is we have a sample of a great variety of manufacturing companies producing many different types of product groups which impact differently during their use phase. Therefore, we decided to include a criterion which is relevant to as wider groups of products as possible.

Environmental criteria other than that considered during our research can be connected to products and considered within the development

process. For instance, Dangelico and Pontrandolfo (2010) summarized, from the literature, 76 different characteristics associated with the environmental impacts of products reported elsewhere during the last twenty years, showing the real breadth and scope of products' environmental impacts. However, many of these impacts are too general from the point of view of today's life-cycle methodology.

4.3. Processing of the data

A standardized analysis database in SPSS software was created for rapid collation and analysis of the survey data. The questionnaire responses were codified and entered into a database, and five low-quality, incomplete, or inadequately answered questionnaires were discarded, leaving 56 acceptable samples. Data was analyzed using software SPSS 17.0 including descriptive statistics (means, frequencies and percentages) and contingency tables for recording and analyzing the relations between two categorical variables, and to present multivariate frequency. Furthermore, one-way analysis by ANOVA variance using the post-hoc Tukey HSD test was used to determine the differences between groups of companies regarding industrial branches and to test the differences between groups of companies regarding the year of ISO 14001 acquisition. In those parts of this paper where the results of ANOVA are presented (section 5.1 and 5.2), the F statistic and the p-values are reported in brackets. The T-test was used in order to test the differences when there were only two independent samples (i.e. between firms that had more than 250 employees and those that had fewer than 250 employees). The general criteria for accepting the hypothesis that differences exist was a 95 percent confidence level ($p < 0.05$; two-tailed).

5. Results and discussion

5.1. Consideration of environmental (ecodesign) criteria in product development

The respondents were asked to identify which ecodesign criteria relating to the whole life cycle of a product(s) were taken into account when developing new products. In general, the Slovenian companies most frequently took into account the following environmental criteria: less waste generation during the manufacturing process (94.1 %), less energy use during the manufacturing process (90.2 %), and reducing the material consumption per unit of a product (88.2 %) (Fig. 1). This trend was, at least to some extent, also reflected in the distribution of financial expenditures for environmental protection in Slovenian industry, where waste management represents the main expenditure activity (SORS, 2010). On the other hand, when developing new products, the companies least often took into account the environmental criteria of fewer components to accelerate dismantling and recycling (54.9 %), the

use of recycled packaging materials (55.8 %), and the reduction of packaging materials for more efficient recycling (64.7 %). From these results, it seemed that the criteria relating to process optimization prevailed over more product-oriented strategies. Regardless of the legislation development and market changes, many companies' perception of their environmental impact was relatively narrow and mostly limited to site-specific activities. This result was to some degree comparable with those reported in a study on product ecodesign in the Baltic States' Industries (Belmane et al., 2004). Similar to the Slovenian companies in general, the Baltic States' companies realized most of their improvements within the production phase regarding the categories of less raw material consumption, replacement of hazardous substances, energy efficiency, solid waste reduction, and the reduction of water and air emissions. However, the ecodesign product strategies of Slovenian certified manufacturing companies and those that operate within certain developed countries differed. For example, an analysis of 77 Dutch small and medium enterprises in the metal, wood, plastics, textile, and electronic industrial sectors revealed that, unlike Slovenian companies, their focus was on the recycling of materials, use of recycled materials, and low energy consumption (van Hemel and Cramer, 2002). A similar trend was confirmed by Santolaria et al. (2011) for Spanish companies.

However, the percentage of companies that considered a particular criterion did not necessarily indicate its importance. In addition, different kinds of products have different levels of potential regarding their environmental improvements. Therefore, the criteria were quantified in order to obtain a more precise insight as to which are more important and which are less important, based on a five-point scale, where 1 is "unimportant" and 5 is "extremely important" (Fig. 2). The relevance of some criteria depends on the industrial branch and product characteristics. Fig. 2 shows the average values for the environmental criteria importance for the whole sample (cumulative values for all the industrial branches included), as well as for the three selected branches.

On average, the Slovenian companies considered reduced material consumption per unit of product as the most important environmental criterion (mean: 3.65), followed by waste reduction during the manufacturing process (mean: 3.41), replacement of toxic and hazardous substances (mean: 3.34), and reduced energy consumption during the manufacturing process (mean: 3.29). The criteria assessed as least important were the use of recyclable materials, increasing the content of recycling materials, several possibilities concerning the environmental optimization of packaging, and reduced water use during the manufacturing process. Water is not an input for every technological process, which is probably the reason for its lower average importance. However, reducing water emissions was given relatively high importance (mean: 2.90).

At first glance, it may seem surprising that the reduction of material consumption had such a high priority for the sampled manufacturing enterprises. However, these findings do link with a report published by the European Commission that investigated the behaviors and attitudes of European SMEs toward the development and uptake of eco-innovations, as a response to the rising prices of natural resources and resource scarcity (Survey EC, 2011). This report found that three-quarters of SMEs businesses had experienced an increase in material costs over the previous five years and 26 percent of respondents said material costs for their company had increased dramatically.

What was surprising in the presented study was the finding that recycling policy is still unrecognized as an important criterion during product development amongst Slovenian manufacturing companies. Although the companies being studied had to develop their own environmental policies because of the ISO 14001 requirements, it seemed that recycling was still not amongst the important aspects of these policies. A comparison of the results from Fig. 2 with those obtained in the previous study (Radonjič and Tominc 2006), where the impact and significance of ISO 14001 certification on the adoption of new production technologies in Slovenia was studied, showed similar results: increasing the share of recycled materials in production processes was the second least-important indicator amongst eight. In contrast, the research carried out by Babakri et al. (2004), which encompassed certified industrial companies that operate within the US, showed that their recycling performance had been significantly and positively affected by ISO 14001 certification.

Various industrial branches and their products are differently affected by legislative requirements, and the environmental impacts of different production technologies vary. A comparison of the average cumulative results (for all branches) with the three selected industrial branches revealed that those firms operating within chemical and related industries indicated lower-than-average importance for almost all the criteria, the exceptions being the criteria of less water emissions and less emissions into the air. On the other hand, firms that operate in the electrical and electronic equipment production and metal industries indicated higher-than-average importance for almost all the criteria (Fig. 2).

The chemical and related industries are more prone to consider important the criteria regarding the process aspects of production, such as water and air emissions and efficient energy use. What was surprising was that the replacement of toxic and hazardous substances received higher priority from the other two industrial branches than from the chemical and related industries.

One possible explanation would be that Slovenia's chemical industry had already substituted hazardous chemicals to a greater extent before the

period 2004-2009, which was taken into account during this research.

The so-called Green Chemistry is becoming a clear trend in the global chemical industry (Warner et al., 1994). Another reason that manufacturers of electrical equipment and household appliances considered the substitution of toxic and hazardous substances as important is the EU legislation (Directive on waste electrical and electronic equipment, Ecodesign directive on energy-using products, Restriction of hazardous substances directive) which is directly related to those kinds of product. This regulation was probably the main driver for the much higher than average importance of fewer components for accelerating the dismantling

and recycling, and the lower energy consumption of the product during its use.

The latter criterion has already become one of the most important aspects of market competitiveness for such products. As Tukker et al. (2000) concluded that, within major EU industries, the electronics industry (together with the motor vehicle and packaging industries) was distinguished as a leader in product ecodesign applications more than ten years ago. It is exactly towards these sectors that the strong requirements by EU environmental end-of-life regulations were directed. For the Slovenian metal industry, increasing the content of recycled materials was relatively important (Fig. 2).

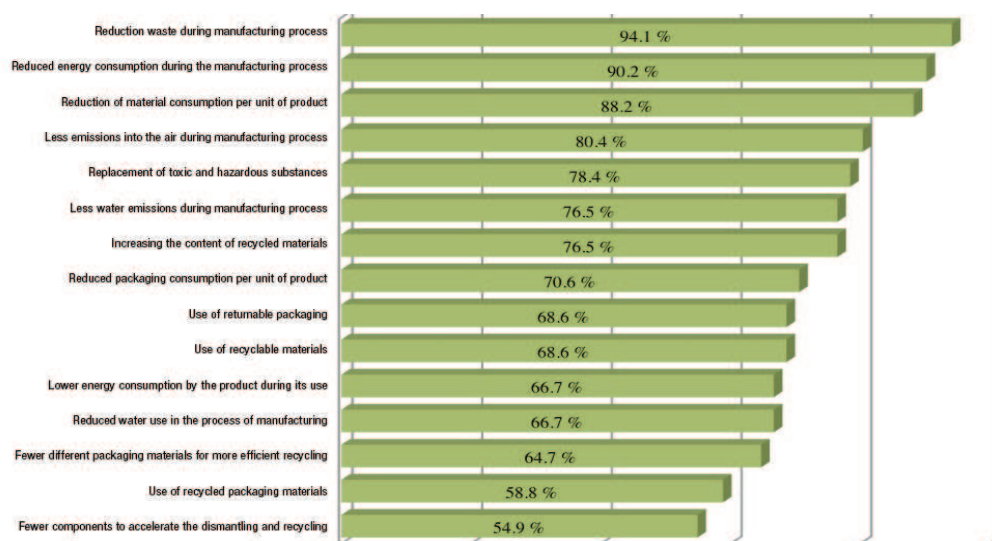


Fig. 1. Percentage of firms that used the environmental (ecodesign) criteria

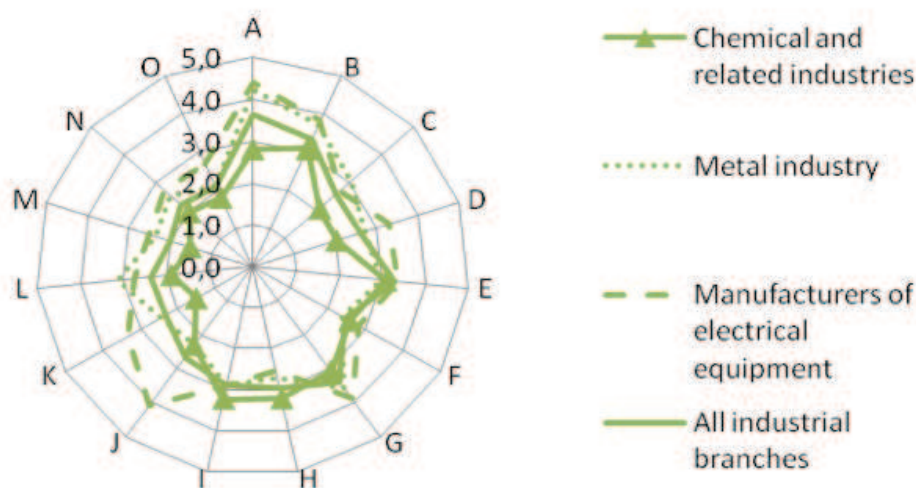


Fig. 2. The importance of environmental (ecodesign) criteria considered within the new product development process (1 – unimportant, 2 – less important, 3 – important, 4 – very important, 5 – extremely important); (Legend: A= Reduced material consumption per unit of product; B= Replacement of toxic and hazardous substances; C= Increase in the content of recycled materials; D= Use of recyclable materials; E= Reduced energy consumption during the manufacturing process; F= Reduced water use in the process of manufacturing; G= Reduced waste during the manufacturing process; H= Less emissions into the air during manufacturing; I= Less water emissions during manufacturing; J= Lower energy consumption by the product during its use; K= Fewer components in order to accelerate dismantling and recycling; L= Reduced packaging consumption per unit of product; M= Use of recycled packaging materials; N= Use of returnable packaging; O= Fewer different packaging materials for more efficient recycling)

A comparison of these findings with the previous results of Radonjič and Tominc (2007) suggested that recycling was growing in importance within Slovenian metal industry, although this could not be claimed for industry in general. Packaging consumption reduction per unit of a product was another point of deviation.

A comparison of the average results for all industries showed that this criterion was of concern primarily for firms in the metal industry and firms that manufacture electrical and electronic equipment, whilst firms in the chemical and related industries were likely to overlook it. This result was also surprising, since the chemical and related industries are amongst the more important users of packaging.

The results from the one-way analysis of variance (ANOVA) on the importance of environmental criteria confirmed that statistically significant differences between different industrial branches existed in three criteria: reduced material consumption per unit of product ($F = 2.6$; $p < 0.05$), lower energy consumption of the product during its use ($F = 2.3$; $p < 0.05$), and fewer components for accelerating the dismantling and recycling ($F = 2.7$; $p < 0.01$). A T-test used to analyze differences in the importance of environmental criteria based on a firm's size showed that there were statistically significant differences between medium-sized and large firms regarding five criteria: reduced water use during the manufacturing processes ($F = 1.6$; $p < 0.05$), lower energy consumption of the product during its use ($F = 0.6$; $p < 0.05$), reduced packaging consumption per unit of product ($F = 1.6$; $p < 0.01$), use of returnable packaging ($F = 2.5$; $p < 0.05$), and fewer different packaging materials for more efficient recycling ($F = 1.1$; $p < 0.01$). For all these environmental criteria, the average importance was higher for large firms than for medium-sized firms. More detailed statistical analyses are given in Appendix 1 and 2.

5.2. Significance of ISO 14001 certification for new product development

Forty-four percent of the analyzed companies had obtained their first ISO 14001 certification in 2000 or earlier. Within this group, 28 percent had obtained certification in 2000, whilst 36 percent acquired ISO 14001 certification between 2001 and 2004, and 20 percent between 2005 and 2008 (Fig. 3). After implementing EMS according to ISO 14001, 9.1 percent of the certified responding enterprises considered the ISO 14001 standard as a necessary condition for successful environmental product design, whilst 38.2 percent saw it as a very useful tool, and 47.3 percent said that it is just a useful tool.

Only 5 percent of the firms thought that the standard was unimportant (Fig. 3). Whilst product development is not the main focus of ISO 14001 (as explained in Chapter 2), it does provide guidance for

the establishment of EMS that can be broadened in connection with product design and development. Even so, the majority of the studied companies considered ISO 14001 only as a useful tool for incorporating the environmental aspects of product design. Further analysis showed that all the companies that saw ISO 14001 certification as a necessary condition for successful product ecodesign belonged to the group of electrical equipment and household appliances manufacturers. The majority of respondents that considered ISO 14001 certification a very useful tool were from the metal industry (62 %), whilst the majority of respondents that considered ISO 14001 certification as only useful were from the chemical and related industries (89 %). In a previous study that investigated the significance of ISO 14001 for the adoption of new and/or modified technology in Slovenian industry, a much higher percentage of respondent companies described it as a very useful tool (63 %), and only 1.4 percent as an unimportant tool (Radonjič and Tominc, 2006).

Results published by various authors on similar topics have shown that the impact of EMS on enhancing product innovation can vary considerably. Rehfeld et al. (2007) found that the certification of EMS had a significantly positive effect on environmental product innovation in German companies, and Ziegler and Rennings (2004) reported that certification according to ISO 14001 had some positive effects on environmental product and process innovations. On the other hand, a weaker relationship between ISO 14001 certification and product eco-innovation was found by Schylander and Martinuzzi (2007), Wagner (2008), Johnstone and Labonne, (2009), and Kautto, (2006). In Kautto's paper, which describes the situation in the Finnish electrical and electronic industries, one of the country's leading innovative branches, more than 83 percent of respondents answered that EMS was not essential in product development because it was seen as too rigid and process-oriented for the extremely dynamic nature of product development.

The conclusion from a review of the presented studies suggested that, instead of a clear causal relation between EMS and product eco-innovation activities, a complex dynamic interrelationship was more likely. These results are state- and branch-specific, so further investigations are needed in order to better understand the differences between the branches. In connection with these findings, organizing the systematic environmental improvement of products is usually more complex and more difficult than organizing systematic improvement of production processes.

Table 3 shows how the acquisition of ISO 14001 certification and the consideration of ecodesign criteria are interrelated. In Table 3, each ecodesign criteria consideration is expressed as a frequency for a certain period (a year) when companies obtained ISO 14001 certification for the first time.

Three of the most frequently used environmental criteria, regardless of the year of ISO 14001 certificate acquisition, were waste reduction during the manufacturing process ($F = 43$), reduced energy consumption during the manufacturing process ($F = 40$), and reduced material consumption per unit of product ($F = 40$). On the other hand, the environmental criteria to which firms gave the least attention were fewer components for accelerating dismantling and recycling ($F = 25$), and use of recycled packaging materials ($F = 27$).

With respect to individual criteria, Table 3 indicates that companies that acquired ISO 14001 earlier tended to incorporate recycled materials into product development more intensively than those with shorter established environmental policies ($p < 0.05$).

The criteria of increasing the content of recycled materials was used more often by firms that had had ISO 14001 certification for a longer period of time (54.3 % of all firms that obtained a certificate in 2000 or earlier) than by firms that had had ISO 14001 certification for a shorter period of time (17 % of firms that were certified between 2005 and 2008). This result was in complete accordance with the findings of Babakri et al. (2004), whose study revealed the same trend for US companies.

In companies that had acquired ISO 14001 certification later (2005–2008 period), reduced energy consumption during the manufacturing process was the most frequently mentioned criterion. This approach is characteristic for companies in the earlier stages of environmental policy, when attention is focused on processes rather than products.

The same is probably true for the replacement of toxic and hazardous substances criterion, which is more important for companies in the earlier stages of environmental policies than for those with longer environmental traditions.

The latter had probably already—and to a greater extent—substituted harmful substances with more environmentally friendly substances. Waste reduction during the manufacturing process was the most frequently reported environmental criterion, regardless of the time of ISO 14001 certification.

This finding was in complete accordance with the results reported by Franchetti, (2011), who investigated ISO 14001 certified manufacturing companies in the US. Again, it is another criterion that is focused on process rather than on final products. In addition, the reduced material consumption per unit of product was considered as one of the most important criteria, regardless of the time of ISO 14001 certification.

This criterion is directly related to manufacturing costs, just as is reduced energy consumption during the manufacturing process, which also ranked high on the list. It can be concluded that the majority of certified Slovenian manufacturing companies continue to focus on process optimization rather than on the real ecodesigning of their products. Of course, this is a generalization for a whole manufacturing sector, and there are likely to be many exceptions.

Comparison based on the period of the first ISO 14001 certificate acquisition showed that companies in the early stages of the EMS environmental policy activities had not developed their efforts towards minimizing the environmental impact of their products to the extent that firms with more experience had.

Some companies that had just begun to address environmental issues tended to have started doing so by using more emission-oriented environmental measures and had later proceeded step-by-step to more advanced environmental strategies, including the development of environmentally-friendly products.

Improvements in manufacturing industries are often very gradual, especially within large enterprises. For example, reducing energy consumption by 10 or 20 percent is a different challenge for a small company than for a large one, and it is different for a large enterprise operating within a primary rather than in a secondary (processing) industrial sector (Radonjič and Tominc, 2006). Furthermore, organizing the systematic environmental improvement of products is usually more complex and more difficult than organizing systematic improvement of production.

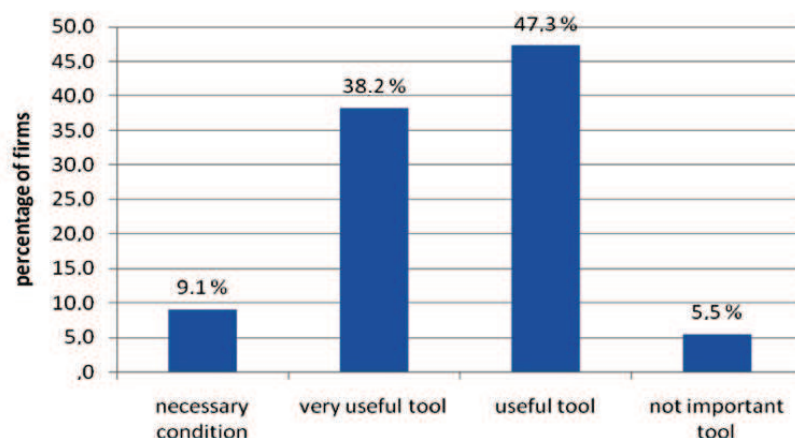


Fig. 3. Significance of ISO 14001 certification on the ecodesign of new products

Table 3. Contingency table for the period of ISO 14001 certificate acquisition in connection with environmental (ecodesign) criteria in product development (f=frequency; χ^2 =chi square; p= significance of differences between groups)

	Period of ISO 14001 certificate acquisition				χ^2 (p)
	2000 and earlier	2001-2004	2005-2008	Total	
<i>Environmental criteria</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	
Reduced material consumption per unit of product	18	14	8	40	146.2 ($p>0.05$)
Replacement of toxic and hazardous substances	16	12	7	35	119.1 ($p>0.05$)
Increase in the content of recycled materials	19	10	6	35	173.1 ($p<0.05$)
Use of recyclable materials	14	13	5	32	135.1 ($p>0.05$)
Reduced energy consumption during the manufacturing process	17	14	9	40	134.8 ($p>0.05$)
Reduced water use in the process of manufacturing	14	10	6	30	86.8 ($p>0.05$)
Reduced waste during the manufacturing process	18	17	8	43	157.9 ($p>0.05$)
Less air emissions	17	13	6	36	137.1 ($p<0.05$)
Less water emissions	17	11	6	34	125.4 ($p<0.05$)
Lower energy consumption by the product during its use	17	9	5	31	108.3 ($p>0.05$)
Fewer components in order to accelerate dismantling and recycling	14	8	3	25	151.8 ($p<0.01$)
Reduced packaging consumption per unit of product	18	13	3	34	77.7 ($p>0.05$)
Use of recycled packaging materials	15	9	3	27	144.8 ($p<0.5$)
Use of returnable packaging	18	12	3	33	143.2 ($p<0.1$)
Fewer different packaging materials for more efficient recycling	16	13	2	31	65.7 ($p>0.05$)

6. Conclusions

Manufacturing companies are faced with additional requirements in terms of environmental criteria which have to be taken into consideration before and during product development process. An environmental management system certified according to the requirements of ISO 14001 standard can help integrate environmental considerations within an organization's overall management system.

The presented study was intended to provide a more precise view on product ecodesign approaches, on one hand, and the possible existence of relation between ecodesign and the ISO 14001 certification of medium and large manufacturing companies operating in the Republic of Slovenia, on the other. The main contribution of this paper is twofold: (a) compared to other related studies it brings some further insight as to which ecodesign criteria based on life cycle approach are used by manufacturers as part of their declared environmental policies, and (b) to reveal whether there is the promotion of ecodesign measures as a result of adopting ISO 14001 certification or not.

Several trends based on the use of ecodesign practice within different manufacturing branches emerged from the study. The companies investigated directed most of their product development attention to waste and energy reduction during the manufacturing process, the reduction of material consumption per unit of product, reducing air and water emissions, and the replacement of toxic and hazardous substances.

Regardless of the legislative developments and market changes, many companies had a

relatively narrow perception of their environmental impacts, which was mostly limited to site-specific activities.

Reduction of material consumption per unit of product was the most important ecodesign criterion for Slovenia's ISO 14001 certified manufacturing companies, whilst less attention was paid to end-of-life issues like recycling. Criteria regarding packaging optimization were given the lowest priorities. Evaluating the reasons for this fact requires further research.

Different industrial branches revealed some important differences regarding their ecodesign preferences (confirming hypothesis 1). In particular, the metal industry and manufacturers of electronic and electrical equipment were more interested in reducing material consumption and in the use of recyclable materials than were those in the chemical and related industries. Because of the EU legislation on energy-using products and on waste electrical and electronic equipment, Slovenian manufacturers had begun giving lower energy consumption and fewer components for accelerating recycling, higher than average priority.

One of the questions concerning our research was whether certified EMS according to ISO 14001 can be a framework for accelerated product ecodesign activities and how the acquisition of ISO 14001 certification is interrelated with the ecodesign criteria.

The results obtained indicated that most Slovenian manufacturing enterprises consider ISO 14001 standard a very useful or useful tool in helping them to accelerate and establish product ecodesign activities (confirming hypothesis 2). Finally, the

results suggested that those companies that acquired ISO 14001 earlier had more intensively incorporated recycled materials into their product development than had those with shorter established environmental policies. In companies that acquired ISO 14001 certification later (during 2005–2008 period), reduced energy consumption during the manufacturing process criterion was the most frequently cited. Such a policy is characteristic for companies in the earlier stages of environmental policy where attention is focused on the processes rather than on the products. These results confirmed hypothesis 3.

In general, the study showed that for the analyzed companies' product ecodesign was surprisingly strongly connected to those established EMS's certified according to ISO 14001 requirements. This was contrary to some previous findings by other authors, as described in Chapter 2. However, it is necessary to be aware that EU environmental regulations and market interest are developing rapidly and new requirements for manufacturers have come into force during recent years. Therefore, when comparing different studies it is essential to consider which time period has been taken into account when carrying out an analysis. Although our findings indicated that certain positive correlations seem to exist at least at some level between EMS and product ecodesign activities within Slovenian manufacturing medium and large companies, more precise causal relations between them would require some further investigation. Namely, various organizational, market, and regulatory motivation and barrier factors influence product ecodesign. This last topic is now already part of our on-going research and will be published in the near future.

The results presented require certain comments regarding the limitations of our study. Namely, there were significant differences amongst the analyzed firms in terms of their sizes, industrial sectors, market orientation, and product characteristics. The results included in this paper represent statistical values for all industrial branches and should be regarded as generalizations of the topic under investigation.

Furthermore, we do not claim that the Slovenian experiences are fully representative of what is going on in other parts of the industrialized world. However, even these indicative conclusions help us to understand product ecodesign trends within a developing country.

We are aware that Slovenia has a small economy with a high proportion of small enterprises, which were not included in our study for the reasons already mentioned. Therefore, the researched findings can not be generalized in regard to all ISO 14001 certified manufacturing companies. However, we would like to stress that the sample of large and medium-sized enterprises was representative and we further analyzed only those three sectors that had the largest proportions within the sample. Similar

research questions could be extended to small enterprises for determining whether there are significant similarities or differences, which represents a challenge for further research.

As with any other investigation, our study left out certain related topics which will have to be investigated in future research. Namely, the results presented in this paper concerning the significance of EMS with respect to ecodesign do not indicate the priorities within the certified environmental policy of the company.

This means, the study did not provide the information as to what importance is given to ecodesign in comparison with other environmental protection activities. Also, a question which remains for further research is whether these companies would have introduced such product changes without the implementation of the ISO 14001 certification.

To conclude, the general areas of knowledge required to carry out ecodesign within EMS in practice should be:

- the assessment of the products' impacts, and identification of appropriate design measures for reducing any adverse effects of these impacts,
- management of product design and development activities to implement these design measures, in order to improve the environmental performance of the products, and
- establishing those conditions by which ecodesign activities and the management of them fit within an EMS.

Acknowledgement

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Appendix

1. Detailed statistics of the one-way analysis of variance (ANOVA) on the importance of products environmental criteria.

ANOVA						
		Sum of Squares	df	Mean Square	F	Sig.
Reduced material consumption per unit of product	Between Groups	5.230	1	5.230	2.669	.041*
	Within Groups	69.849	49	1.425		
	Total	75.079	50			
Replacement of toxic and hazardous substances	Between Groups	3.696	1	3.696	1.626	.208
	Within Groups	111.384	49	2.273		
	Total	115.080	50			
Increase in the content of recycled materials	Between Groups	.805	1	.805	.523	.473
	Within Groups	75.432	49	1.539		
	Total	76.237	50			
Use of recyclable materials	Between Groups	5.528	1	5.528	2.933	.093
	Within Groups	92.357	49	1.885		
	Total	97.885	50			
Reduced energy consumption during the manufacturing process	Between Groups	1.580	1	1.580	1.545	.220
	Within Groups	50.100	49	1.022		
	Total	51.680	50			
Reduced water use	Between Groups	9.088	1	9.088	5.701	.061

during manufacturing process	Within Groups	78.113	49	1.594		
	Total	87.202	50			
Reduced waste during the manufacturing process	Between Groups	3.788	1	3.788	3.304	.075
	Within Groups	56.171	49	1.146		
	Total	59.958	50			
Less emissions into the air	Between Groups	.113	1	.113	.060	.808
	Within Groups	93.098	49	1.900		
	Total	93.211	50			
Less water emissions	Between Groups	3.657	1	3.657	1.667	.203
	Within Groups	107.467	49	2.193		
	Total	111.123	50			
Lower energy consumption of the product during its use	Between Groups	8.810	1	8.810	2.275	.044*
	Within Groups	100.971	49	2.061		
	Total	109.780	50			
Use of recycled packaging materials	Between Groups	1.439	1	1.439	.769	.385
	Within Groups	91.711	49	1.872		
	Total	93.150	50			
Reduced packaging consumption per unit of product	Between Groups	11.620	1	1.620	1.835	.091
	Within Groups	48.109	49	.982		
	Total	59.730	50			
Use of recycled packaging materials	Between Groups	1.096	1	1.096	.901	.347
	Within Groups	59.565	49	1.216		
	Total	60.660	50			
Use of returnable packaging	Between Groups	11.035	1	11.035	9.861	.073
	Within Groups	54.831	49	1.119		
	Total	65.865	50			
Fewer different packaging materials for more efficient recycling	Between Groups	11.201	1	11.201	2.726	.001*
	Within Groups	41.341	49	.844		
	Total	52.542	50			

2. T-test values related to differences of environmental product criteria importance.

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means		
		F	Sig.	t	df	Sig. (2-tailed)
Reduced material consumption per unit of product	Equal variances assumed	8.006	.007	-1.915	49	.061
	Equal variances not assumed			-2.053	46.303	.046
Replacement of toxic and hazardous substances	Equal variances assumed	.228	.635	-1.275	49	.208
	Equal variances not assumed			-1.281	46.106	.207
Increase in the content of recycled materials	Equal variances assumed	.012	.913	-.723	49	.473
	Equal variances not assumed			-.712	42.479	.481
Use of recyclable materials	Equal variances assumed	1.532	.222	-1.713	49	.093
	Equal variances not assumed			-1.671	40.646	.102
Reduced energy consumption during the manufacturing process	Equal variances assumed	.209	.649	-1.243	49	.220
	Equal variances not assumed			-1.264	47.774	.212
Reduced water use during manufacturing process	Equal variances assumed	1.640	.206	-2.388	49	.021*
	Equal variances not assumed			-2.434	48.005	.019

Reduced waste during the manufacturing process	Equal variances assumed	.426	.517	-1.818	49	.075
	Equal variances not assumed			-1.855	48.086	.070
Less emissions into the air	Equal variances assumed	2.029	.161	-.244	49	.808
	Equal variances not assumed			-.250	48.499	.804
Less water emissions	Equal variances assumed	3.406	.071	-1.291	49	.203
	Equal variances not assumed			-1.329	48.734	.190
Lower energy consumption of the product during its use	Equal variances assumed	.645	.426	-2.068	49	.044*
	Equal variances not assumed			-2.035	42.411	.048
Fewer components in order to accelerate dismantling and recycling	Equal variances assumed	.001	.980	-.877	49	.385
	Equal variances not assumed			-.874	44.835	.387
Reduced packaging consumption per unit of product	Equal variances assumed	1.630	.208	-3.440	49	.001*
	Equal variances not assumed			-3.512	48.127	.001
Use of recycled packaging materials	Equal variances assumed	.660	.420	-.949	49	.347
	Equal variances not assumed			-.947	44.967	.349
Use of returnable packaging	Equal variances assumed	2.534	.118	-3.140	49	.003*
	Equal variances not assumed			-3.004	36.570	.005
Fewer different packaging materials for more efficient recycling	Equal variances assumed	1.147	.289	-3.644	49	.001*
	Equal variances not assumed			-3.538	39.634	.001

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ESTIMATING CROWN CLOSURE OF FOREST STANDS USING LANDSAT TM DATA: A CASE STUDY FROM TURKEY

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Abstract

Remote sensing data has been broadly used in assessing and monitoring natural resources. Monitoring forest resources with Landsat Thematic Mapper (TM) and other fine resolution sensors has become a challenging work in a wide variety of forest applications. In this paper, the relationships between stand crown closure with spectral reflectance values and some vegetation indices (VIs) obtained from Landsat TM were investigated in a case study area. The Pearson correlation and multiple regression analysis were used to estimate the crown closure. The regression analysis showed that a linear combination of Soil Adjusted Vegetation Index (SAVI), normalized difference 32 index (ND32) and normalized difference 57 index (ND57) are better predictors for estimating crown closure (adjusted $R^2=0.757$; root mean square error (RMSE)=2.5304%) than other TM bands (adjusted $R^2=0.529$; RMSE=4.0782%). The Pearson correlation analysis results demonstrated that NDVI, Simple ratio (SR), Difference Vegetation Index (DVI), Transformed Vegetation Index (TVI), Soil Adjusted Vegetation Index (SAVI) had the highest positive correlation ($r=0.84$) and Infrared Percentage Vegetation Index (IPWI) had the negative correlation ($r=-0.84$) with crown closure measurements. Furthermore, the TM 4 band showed the highest correlation ($r=0.64$) with crown closure between TM 1-5 and TM 7. This research concluded that forest managers could use Landsat TM imagery for estimating crown closure used for generating maps in developing forest management plans.

Key words: Landsat TM, regression analysis, stand crown closure

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1. Introduction

Forest management planning requires data to characterize different aspect of forest stands. Although various attributes can be used to characterize stands, few properties such as development stages, species mix, crown closure and site index are widely used in forest management activities. Among them, stand crown closure is a major factor for assessing stand structure and a significant indicator in determining forestry applications.

It is extensively used in both forest research and forest management planning and a valuable attribute of forest inventory that plays a significant role in forest ecosystem management (Fiala et al.,

2006). Furthermore, the crown closure is used to estimate the penetration level of lights to the understory vegetation (Canham et al., 1990; Englund et al., 2000; Lieffers et al., 1999).

In Turkey, forest stands are defined and classified by differences in species composition, development stages and crown closure aside from site quality. The crown closure is described as the percentage of forest canopy projected to a horizontal plane over a unit ground area and becomes a very important parameter in developing forest models such as ecological, hydrological and climatic models (Xu et al., 2003).

For example, the ecological conditions like surface reflection, rainfall interception and light penetration through the canopy, are dependent on the

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contents of crown closure (Roy et al., 1996). However, its measurement in the field is relatively difficult, particularly time consuming and expensive (Pu et al., 2003; Xu et al., 2003). Remote sensing is an alternative method to the field measurements in accurate estimation of crown closure, because satellite data has been considered a low-cost and large-area coverage forest information sources (Franklin et al., 2003). Applications of remote sensing in forest resources are commonly presented in four categories; classification of land use/forest cover, estimation of forest inventory parameters, detection of forest change over time, and provision of data to forest modeling (Foody, 2002; Franklin, 2001; Hyypä et al., 2000).

Remote sensing applications play a vital role in meeting information needs for ecosystem-based forest management planning activities (Franklin, 2001). Several forest inventory variables such as crown closure, age, leaf area index (LAI) and development stages, however, are critical inputs to some climate and ecological models (Liang, 2004). In this context, remote sensing data provides us with a powerful means to monitor the spatial and temporal structure of forest ecosystems.

Generally, remote sensing data can be used in forest ecosystem inventory to reduce the amount of field work (Yeşil et al., 2002). Observing forest attributes with Landsat TM and other fine resolution sensors is a crucial process in a extensive variety of forest applications. The attractiveness of Landsat satellite image can be qualified to several basic features of the Landsat program, including low imagery costs and free data distribution that facilitates widespread use of a sensor whose spatial resolution is sufficient to describe typical forest cover dynamics related to forest management (Cohen and Goward, 2004).

The spectral response of forest composition and structure is quite informative in classifying forest ecosystems. For example, several VIs were developed to identify forest crown closure (Roy et al., 1996). VIs reflects the association between the low reflectance in the visible region of the electromagnetic radiation with the high reflectance in the near infrared region (Rondeaux et al., 1996; Tucker 1979).

Thus, the VIs are designed from mixtures of several spectral values that are mathematically recombined to produce a single value indicating the amount of vegetation biomass within a pixel (Campbell, 1996).

Normalized difference vegetation index (NDVI) is the most preferred one for analyzing forest vegetation structures as it provides good information on crown closure in coniferous forest areas. It was described to vary with vegetation activities in dry or moist deciduous forest areas (Roy and Ravan, 1994). The VIs such as NDVI, SAVI, SR and EVI based on mixtures of two or more spectral bands, were formulized to gather more information about the vegetation and its properties (spatial forest structure,

crown closure, volume, biomass productivity, etc.) that can be detected more accurately from a multi-band analysis than from a single band analysis (Bannari et al., 1995). Also, stand crown closure is significant auxiliary variable in the prediction of LAI using empirical or physically based vegetation reflectance models (Jasinski, 1990; Knyazikhin et al., 1998; Kuusk and Nilson, 2000; Nilson and Peterson, 1991; Spanner et al., 1990). Given the fact that crown closure is a good estimator of stand structure and can be detected with remote sensing, Landsat TM data were used to explore the relationships. Therefore, this study was designed to investigate the relationship between band reflectance values recorded and VIs calculated by Landsat TM sensor to estimate the crown closure of the stands.

2. Study sites and data

The study area is located in the Kızılcaasu Planning Unit covering 7950 ha in the middle Black Sea Region of Turkey (513595-526360 E, 4618958-4631748 N, UTM ED 50 datum Zone 36 N) (Fig. 1). Average slope of the study area is about 38%. The altitude ranges from 240 m to 1500 m above sea level. Forest vegetation consists of Oriental beech (*Fagus orientalis* Lipsky), fir (*Abies nordmanniana* (Stev.) Spach subsp. *nordmanniana*), Scots pine (*Pinus sylvestris* L.), Common hornbeam (*Carpinus betulus* L.), Black pine (*Pinus nigra* L.), Oak species, and *Platanus orientalis*. Mean annual temperature of the study area is about 13.4°C and mean annual precipitation is 1229.5 mm. Main soil types are sandy clay loam and clay loam.

Two kinds of remotely sensed image data were used in this study. First was the moderate resolution image from Landsat TM acquired on August 15, 2008 and the second image was the high spatial resolution satellite image from QuickBird acquired on September 6, 2008. The first six bands of visible (TM 1, TM 2, TM 3), NIR (TM 4) and MIR (TM 5 and TM 7) data of the Landsat TM sensor with 30 m spatial resolution along with the blue, red, green and near infrared bands of QuickBird sensor with a spatial resolution of 0.6 m were used. Furthermore, 1:25.000 scale forest cover type map for 2008 and 1:25.000 scale topographical maps were used in this research.

Planning process begins with a forest inventory based on both remote sensing data and ground surveys. As for the ground measurements, a total of 699 sample plots in the summer of 2008 as part of timber cruising were established with 300 x 300 m grids and the necessary measurements were taken in each sample plot. All sample plots were taken in forest areas.

In each sample plot, diameter at breast height (dbh) was measured to the nearest 0.1 cm with calipers for every living tree over 7.9 cm and total tree height was measured to the nearest 0.1 m with digital hypsometer in randomized sub-samples.

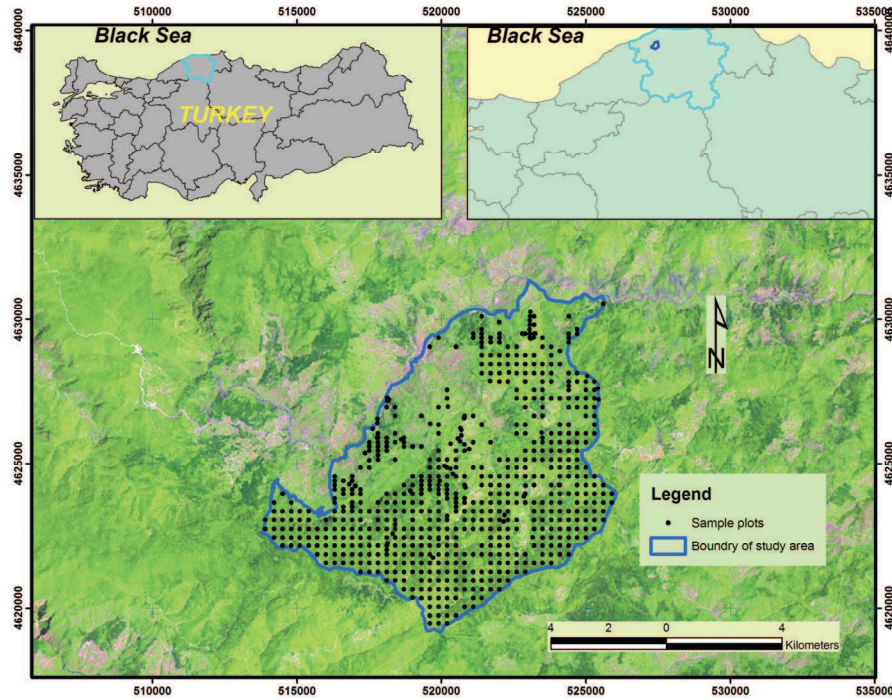


Fig. 1. The geographic location of the study area

The classical inventory measurements calculated for each sample plot are the dominant heights (selected from 100-dominant and co-dominant highest trees per hectare), stand volume per hectare, basal area per hectare, tree density per hectare and the quadratic mean diameter.

Development stages and crown closures are required in preparing forest management plans. Particularly though, crown closure is also used to determine the size of sample plot in field survey according to forest management guidelines in Turkey. The sizes of sample area are pre-determined to vary from 400 m², 600 m² to 800 m² depending on crown closure. For example, 400 m² plot size is taken in full crown closure.

3. Methods

Landsat TM and QuickBird satellite data were orthorectified and georeferenced to UTM Zone 36 projection based on the European Datum 50 using first order nearest neighborhood rules. Its accuracy was checked with 1:25.000 scaled topographical maps and GPS data obtained from the field, both of which proved the accuracy of the rectification. A total of 25 ground points were used to register the Landsat TM and QuickBird images with a rectification error less than 1 pixel image. Data processing, interpreting and analysis were performed using Erdas Imagine 9.1TM version (Erdas, 2002). The training ground data set was obtained from the forest cover type map and a fine spatial resolution land cover classification (maximum likelihood classification) of QuickBird satellite image. Particularly, this classification was clumped to

estimate stand crown closure at the Landsat TM satellite image. The predictor variables contained the Landsat TM bands (except for Band 6) and fourteen VIs calculated the Landsat TM. The QuickBird image with a spatial resolution of 0.6 m was used to subtract reference percentage stand crown closure data required to train in the study area. The QuickBird image acting different forest cover types were classified and detailed to forest and non-forest pixels. Later, the classification results were transformed to estimate percentage stand crown closure at the Landsat TM. In the past years, several studies to predict percentage crown closure as a continuous variable have been conducted by multiple linear regression (Berberoğlu et al., 2009; DeFries et al., 2000), a linear mixture model (Iverson et al. 1989) and regression tree modeling (Hansen et al., 2003). In this study, the Linear mixture modeling (LMM) fuzzy classification method was used to determine the stand crown closure. The LMM is based on the presumption that class mixing is achieved in a linear manner. This adopts a minimum squares method to predict the class proportions within each pixel. The fact is that a permanent scene can be modeled as the total of the radiometric coactions among cover types weighted by their relative proportions (Graetz, 1990). The structure of the mixture model is depicted in (Eq. 1).

$$DN_i = \sum_{c=1}^n \int_{ic} (DN_i)_{ic} + \varepsilon_i \quad (1)$$

where, DN_i is the reflectance value of a pixel in waveband i , $\int_{ic}$ is the pure pixel function of the cover type, c , to be calculated for each band, n is the band

number, $(DN)_{ic}$ is the spectral contribution of cover type c and ε_i is the error term. Fine spatial resolution (0.6m) QuickBird data was classified using MLC (maximum likelihood classifier) to identify forest and non-forest areas. The result was rescaled to Landsat TM data (30m spatial resolution) to obtain training and testing dataset so that 1 Landsat pixel could be covered with the mean of 2500 QuickBird pixel values (tree canopy cover). The flowchart of estimation the stand crown closure was depicted in Fig. 2 and the crown closure map obtained from the LMM was illustrated in Fig. 3.

The map in Fig. 3 indicates five crown closure classes. Four of these classes (21-100%) consist of forest area; the other (0-20%) consists of non-forest areas.

3.1. Calculating VIs

In this study, Landsat TM data were used to produce fourteen VIs such as NDVI, SR, DVI, TVI, NLI, SAVI, ND53, ND54, ND57, ND32, ND73, NDWI, EVI and IPWI. The formulas and references for VIs were shown in Table 1.

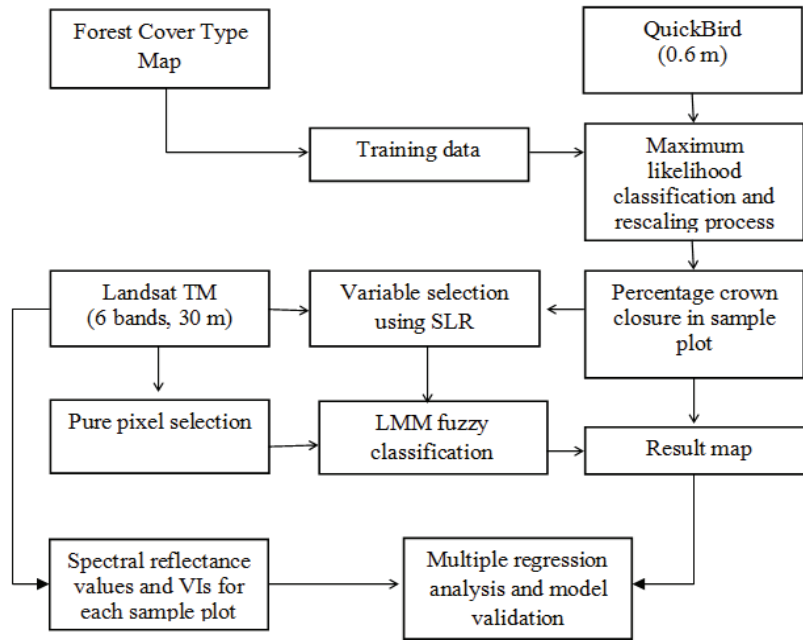


Fig. 2. The flowchart to estimate the crown closure

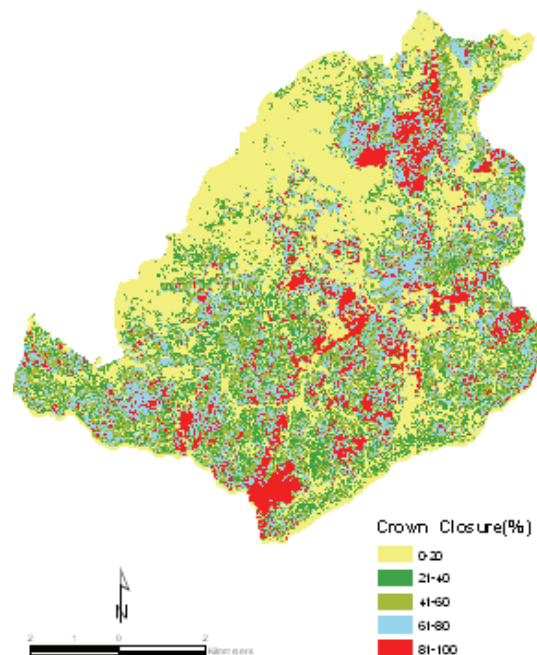


Fig. 3. Crown closure map based on fuzzy classification method

Table 1. Definition of VIs used in the study area

<i>VIs</i>	<i>Formula</i>	<i>Reference</i>
NDVI	$\text{NIR-Red}/(\text{NIR}+\text{Red})$	Rouse et al. (1974)
SR	NIR/Red	Jordan (1969)
DVI	$\text{NIR}-\text{Red}$	Clevers (1988)
TVI	$\text{NIR-Red}/(\text{NIR}+\text{Red}+0.5)$	Deering et al. (1975)
NLI	$\text{NIR}^2-\text{Red}/(\text{NIR}^2+\text{Red})$	Gong et al. (2003)
SAVI	$(\text{NIR}-\text{Red}) \cdot (1+\text{L})/(\text{NIR}+\text{Red}+\text{L})$	Huete (1988)
ND53	$\text{MID-Red}/(\text{MID}+\text{Red})$	Lu et al. (2004)
ND54	$\text{MID-NIR}/(\text{MID}+\text{NIR})$	Lu et al. (2004)
ND57	$\text{MID}(\text{TM}5)-\text{MID}(\text{TM}7)/(\text{MID}+\text{MID})$	Lu et al. (2004)
ND32	$\text{Red-Blue}/(\text{Red}+\text{Blue})$	Lu et al. (2004)
ND73	$\text{MID}(\text{TM}7)-\text{Red}/(\text{MID}+\text{Red})$	Sivanpillai et al. (2006)
NDWI	$\text{NIR-MID}/(\text{NIR}+\text{MID})$	Gao (1996)
EVI	$\text{NIR-Red}/((\text{NIR}+(\text{C}1 \cdot \text{Red})-(\text{C}2 \cdot \text{Blue})) \cdot (1+\text{L}))$	Huete et al. (1999)
IPVI	$\text{NIR}/(\text{NIR}+\text{Red})$	Crippen (1990)

ND, normalized difference; NDVI, Normalize Difference Vegetation Index; SR, Simple ratio; SAVI, Soil Adjusted Vegetation Index; DVI, Difference Vegetation Index; TVI, Transformed Vegetation Index; NLI, Nonlinear Vegetation Index; NDWI, Normalized Difference Water Index; EVI, Enhanced Vegetation Index; IPVI, Infrared Percentage Vegetation Index; VIS, visible wavelengths (red, green, blue); NIR, near infrared wavelengths (TM4); MID, middle infrared wavelengths (TM 5, TM 7)

3.2. Statistical analysis

In this study, Pearson correlation and multiple regression analysis were used to examine the relationships between crown closure and the spectral reflectance values. Fourteen VIs were obtained from Landsat TM satellite image. The crown closure was used as a dependent variable. During the modeling process, Pearson correlation analysis was initially used to analyze the relationships between crown closure and Landsat TM data.

The Pearson correlation matrix was constructed to identify which Landsat TM data variables would indicate the best correlation with crown closure. The Pearson correlation procedure computes Pearson correlation coefficients that define the linear relationship between two variables, e.g. crown closure and relevant Landsat TM data. Secondly, multiple linear regression models were developed to estimate the crown closure as a function of a suite of remote sensing data variables specific to the case study area. In developing multiple linear regression models to present the variation in crown closure, stepwise variable selection method was used. In this method, the process starts out just as in forward selection. At each step, however, variables that are already in the model are first evaluated for removal. If any of them are eligible for removal, then the one with the least R^2 is removed. The Pearson correlation and multiple stepwise regression analysis were performed using SPSS version 15.0 (SPSS Institute Inc., 2008). The stepwise regression technique was used to select the best site variables that are significant ($p < 0.05$) with the highest value of coefficient of determination adjusted by number of parameters (R^2_{adj}), also called the adjusted coefficient of determination. In this study, the following linear relationship was assumed (Eq. 2):

$$SCC = \beta_0 + \beta_1 \cdot X_1 + \beta_2 \cdot X_2 + \dots + \beta_n \cdot X_n + \varepsilon \quad (2)$$

where, SCC is the stand crown closure, variable vectors corresponding to Landsat data, such as spectral reflectance values, TM 1-5 and TM 7, and fourteen VIs variables (X_i), β_i represent model coefficients and ε is the additive bias (Corona et al., 1998; Fontes et al., 2003).

Separate regression analyses were accomplished to compare the predictive power of the spectral reflectance values of TM 1-5 and TM 7 with VIs, using relevant Landsat TM data with two regression models; one model predicting stand crown closure by using the spectral reflectance values and the other for model using VIs. In each sub-group, the related crown closure was predicted by using the spectral reflectance values, e.g. TM 1-5 and TM 7, and VIs to build regression models. A total of 699 sample plots were available for statistical analysis. These sample plots were randomly split into two data sets using the SPSS random number function of "SELECT CASE" (SPSS Institute Inc. 2007): model fitting data and the validation data set. About 80% of total data (559 plots) was used to fit model parameters. The remaining 140 sample plots were reserved for model validation and also calibration response data set.

Estimation of crown closure using the regression models should be statistically significant at 95% probability level. The null hypothesis was tested and parameters that were not significantly different from zero were refused (Fontes et al., 2003). The accuracy statistics covered the absolute and relative biases as well as the root mean square error (RMSE and RMSE %). These statistics were calculated for the models shown in Eqs. (3-6).

$$\text{bias} = \frac{\sum (y_i - \hat{y}_i)}{n} \quad (3)$$

$$\text{bias \%} = 100 \cdot \frac{\sum (y_i - \hat{y}_i) / n}{\sum \hat{y}_i / n} \quad (4)$$

$$RMSE = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n-1}} \quad (5)$$

$$RMSE \% = 100 \frac{\sqrt{\sum (y_i - \hat{y}_i)^2 / (n-1)}}{\sum \hat{y}_i / n} \quad (6)$$

where $\hat{y}_i$ is the estimate; y_i the observed value of y ; and n the number of observations.

To further assess the superiority of the model fit, we used the magnitude and distribution of predicted values versus observed for crown closure using Landsat TM data. We examined any obvious dependencies or patterns representing systematic divergences and a breakdown of assumptions of multiple least-square regressions. The presence of multicollinearity was defined by values of the variance inflation factors (VIFs), with values greater than 5 taken to indicate the presence of multicollinearity (Meyers, 1986). The variables used in this study were provided in Table 2.

3.3. Validation

Model validation was performed based on the difference between observed and predicted values (residual values) using the validation data set. The Wilcoxon rank test from 140 sample plots was evaluated with null hypothesis for mean prediction residual equal to zero. If Wilcoxon rank test reveals that the null hypothesis could not be rejected (residuals statistically not significantly different from zero and so), then the developed models would be statistically suitable for the prediction of crown closure with satellite data variables in the stands under investigation. Wilcoxon rank test about the mean errors for all sub-group models being equal to zero revealed that the null hypothesis could not be rejected and significantly not different from zero.

Thus, these sub-group models with band values and VIs were statistically acceptable and suitable for predicting crown closure.

4. Results

4.1. Correlation between crown closure and Landsat TM data

Table 3 summarizes the Pearson correlation coefficients between the crown closure and the reflectance values, TM 1-5 and TM 7, and fourteen VIs. All VIs and spectral reflectance values (except for TM 2) were significantly correlated with stand crown closure at 95% probability level. The stand crown closure showed the highest correlation with NDVI ($r=0.84$, $p<0.01$), SAVI($r=0.84$, $p<0.01$), SR($r=0.84$, $p<0.01$), TVI($r=0.84$, $p<0.01$) and IPWI($r=-0.84$, $p<0.01$), and displayed the moderate correlation with band spectral reflectance values such as TM 4 ($r=0.64$, $p<0.01$) and TM5($r=0.48$, $p<0.01$).

4.2. Regression equations between crown closure and Landsat TM data

Multiple regression models were developed with Eq. (1) to model crown closure as a function of Landsat TM data variables based on Pearson correlation analysis. The selected best regression subgroup models, accuracy statistics such as coefficients of determination (R^2), the standard error of model ($Sy.x$), bias, bias%, RMSE, RMSE%, Durbin-Watson values, and the error estimates of crown closure are presented for the spectral reflectance values in Table 4 and for VIs in Table 5. In these selected subgroup regression models for crown closure, the F statistics and coefficients were significant at a probability level of 95 percent ($p<0.05$).

Table 2. Mean, minimum, maximum, standard deviation and variance value of the stand characteristics in the study area

Variable	Mean	Min.	Max.	Std. deviation	Variance
Crown Closure	0.66	0.45	0.76	0.041	0.0016
TM-1	66.25	56.00	93.00	3.27	10.72
TM-2	51.25	44.00	83.00	4.40	19.40
TM-3	38.58	31.00	86.00	4.94	24.39
TM-4	100.77	58.00	157.00	16.88	284.97
TM-5	79.81	37.00	127.00	14.35	205.85
TM-7	37.87	22.00	79.00	6.89	47.52
NDVI	0.45	0.14	0.61	0.07	0.005
SR	2.67	1.32	4.11	0.44	5.19
DVI	63.21	20.00	112.00	16.52	272.84
TVI	0.95	0.64	1.11	0.07	0.005
NLI	0.99	0.98	1.00	0.00	0.00001
SAVI	0.67	0.20	0.91	0.10	0.01
ND53	0.35	0.00	0.50	0.08	0.01
ND54	-0.12	-0.25	0.06	0.05	0.002
ND57	0.36	0.25	0.44	0.03	0.001
ND32	-0.14	-0.25	-0.03	0.03	0.001
ND73	-0.01	-0.25	0.19	0.07	0.01
NDWI	0.12	-0.06	0.25	0.05	0.002
EVI	-4.25	-372	-0.55	19.53	381.59
IPVI	0.72	0.57	0.80	0.03	0.001

Table 3. Pearson correlations between crown closure and the spectral reflectance factors, TM 1-5 and TM 7, and 14 VIs

<i>Variables</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>	<i>11</i>	<i>12</i>	<i>13</i>	<i>14</i>	<i>15</i>	<i>16</i>	<i>17</i>	<i>18</i>	<i>19</i>	<i>20</i>	<i>21</i>
(1) Crown Closure	1																				
(2) TM1	-0.19**	1																			
(3) TM2	-0.01ns	0.73**	1																		
(4) TM3	-0.14**	0.72**	0.8**	1																	
(5) TM4	0.64**	0.22**	0.5**	0.23**	1																
(6) TM5	0.48**	0.28**	0.51**	0.41**	0.86**	1															
(7) TM7	0.26**	0.37**	0.56**	0.54**	0.67**	0.90**	1														
(8)NDVI	0.84**	-0.22**	-0.01ns	-0.34**	0.80**	0.61**	0.34**	1													
(9) SR	0.84**	0.17**	0.05ns	-0.29**	0.83**	0.64**	0.39**	0.98**	1												
(10) DVI	0.84**	0.05ns	0.31**	0.03ns	0.97**	0.79**	0.56	0.92**	0.94**	1											
(11) TVI	0.84**	-0.22**	-0.01ns	0.34**	0.80**	0.61**	0.35**	0.99**	0.98**	0.92**	1										
(12) NLI	0.59**	-0.02ns	0.21**	-0.01ns	0.68**	0.53**	0.37**	0.64**	0.66**	0.77**	0.64**	1									
(13)SAVI	0.84**	-0.22**	-0.01ns	-0.34**	0.80**	0.61**	0.35**	0.99**	0.98**	0.92**	0.99**	0.64**	1								
(14)ND53	0.73**	-0.12*	0.05ns	-0.16**	0.74**	0.82**	0.64**	0.86**	0.85**	0.81**	0.86**	0.55**	0.86**	1							
(15)ND54	0.18**	0.15**	0.09ns	0.29**	-0.10*	0.41**	0.54**	-0.23**	-0.23**	-0.18**	-0.23**	-0.15**	-0.24**	0.29**	1						
(16)ND57	0.54**	-0.08ns	0.03ns	-0.13*	0.56**	0.43**	0.01ns	0.63**	0.62**	0.62**	0.63**	0.44**	0.63**	0.55**	-0.14**	1					
(17)ND32	-0.25**	0.27**	0.08ns	0.65**	-0.13*	0.06ns	0.19**	-0.52**	-0.51**	-0.31**	-0.52**	-0.24**	-0.52	-0.32**	0.34**	-0.22**	1				
(18)ND73	0.59**	-0.1*	0.05ns	-0.13*	0.59**	0.75**	0.76**	0.69**	0.69**	0.65**	0.69**	0.43**	0.69**	0.90**	0.42**	0.13*	-0.28**	1			
(19)NDWI	0.18**	0. -0.15**	-0.09ns	-0.29**	0.10*	-0.41**	0.54**	0.23**	0.23**	0.18**	0.23**	0.15**	0.24**	-0.30**	0.99**	0.14**	-0.34**	-0.42**	1		
(20) EVI	-0.15**	-0.03ns	0.02ns	-0.04ns	-0.17**	-0.15**	-0.12*	-0.13*	-0.15**	-0.17**	-0.13**	-0.20**	-0.13*	-0.13**	0.01ns	-0.09ns	-0.01ns	-0.10*	-0.01ns	1	
(21) IPWI	-0.84**	-0.22**	-0.01ns	0.34**	0.78**	0.61**	0.35**	0.99**	0.98**	0.92**	0.99**	0.64**	0.99**	0.85**	-0.23**	0.63**	0.52**	-0.69**	0.23**	-0.13*	1

*Correlation is significant at 0.05 level. **Correlation is significant at 0.01 level. ns: not significant

Table 4. Parameters of the 'best fit' regression models of crown closures based on the spectral reflectance values, TM 1-5 - TM 7

Independent Variables	Coefficients of Independent Variables	S.E. of Variables	t-statistics	p-value	VIF
Constant	0.654132	0.014705	44.4852	0.000	
TM 2	-0.003518	0.000315	-11.1602	0.000	1.2322
TM 4	0.001889	0.000084	22.5457	0.000	1.2322
R ² =0.529	S _{xx} =0.02716	D. W.=1.778	Bias=4.0539	Bias%=6.1006	RMSE=0.0271
					RMSE%=4.0782

R_a²: Adjusted coefficient of determination, S.E.: Standard Error, D. W.: Durbin-Watson value, t statistics is probability values, RMSE: the root mean square error. VIF: variance inflation factor

Table 5. Parameters of the ‘best fit’ regression models of crown closure based VIs

Independent Variables	Coefficients of Independent Variables	S. E. of Variables	t-statistics	p-value	VIF
Constant	0.534729	0.010268	52.0779	0.000	
SAVI	0.329207	0.013582	24.2387	0.000	0.3830
ND32	0.287244	0.035519	8.0870	0.000	0.6537
ND57	-0.140217	0.038750	-3.6185	0.010	0.5141
R ² =0.757 S _{y.x} =0.01681 D. W.=1.944 Bias=3.9307 Bias%=5.9468 RMSE=0.0167 RMSE%=2.5304					

R_a^2 : Adjusted coefficient of determination, S.E.: Standard Error, D. W.: Durbin-Watson value, t statistics is probability values, RMSE: the root mean square error, VIF: variance inflation factor

The crown closure model was developed based on the reflectance values of TM 2 and TM 4 as independent variables, and this model performance was calculated and adjusted with $R^2=0.529$, $S_{y.x}=0.02716$, bias=4.0539, bias%=6.1006, RMSE=0.0271 and RMSE%=4.0782. The crown closure model with VIs were developed by SAVI, ND32 and ND57 as independent variables, and the model performance was calculated and adjusted with $R^2=0.757$, $S_{y.x}=0.01681$, bias=3.9307, bias%=5.9468, RMSE=0.0167 and RMSE%=2.5304. Compared to two different models, the crown closure model with VIs showed the better accuracy statistics than did the model with spectral reflectance values.

In validation process, the Wilcoxon rank test shows that two models including band values and VIs are unbiased. This means that the mean errors from the models are not statistically significantly different from zero, Z value=-0.381, p=0.703 for band values and Z value=-0.422, p=0.673 for h-vegetation index values sub-group model, respectively.

To control for multicollinearity, the variance inflation factor (VIF) values were estimated for each independent variable in the subgroup models. The VIF value is 1.2322 in crown closure model represented by spectral reflectance values. The VIF values ranged from 0.3830 to 0.6537 in the models based on VIs. Since all VIF values were lower than 5 for the subgroups models, there seemed no problem of multicollinearity for the independent variables of these models (Tables 4-5).

5. Discussion

In this study, the stand crown closure demonstrated the highest correlation with NDVI ($r=0.84$), SAVI($r=0.84$), SR($r=0.84$), TVI($r=0.84$) and IPWI($r=0.84$), and displayed the moderate correlation with band spectral reflectance values such as TM 4 ($r=0.64$) and TM 5 ($r=0.48$). Butera (1986) investigated the correlation of crown closure with the TMS bands. He found that the strongest coefficient found for TMS bands, 1, 5, and 7 (0.76, 0.80 and 0.76, respectively) and TMS band 4 ($r=0.14$) was the lowest. Larson (1993) found that NDVI was correlated with crown closure using Landsat TM ($r=0.55$), MSS($r=0.69$) and SPOT HRV XS ($r=0.71$). Franklin et al. (2003) showed the important

relationships between Landsat band values and crown closure for two conifer species *Pinus banksiana* Lamb. and *Picea glauca* (Moench) Vass. He indicated that, for white spruce, the TM4 was strongly related to crown closure and the TM5 was moderately related to crown closure ($r=0.8$ and $r=-0.57$), respectively. Our study demonstrated that the use of VIs, incorporating visible and near-infrared reflectance values, generated relationships similar, in strength, to those accomplished by Franklin et al. (2003) and Xu et al. (2003). In fact, Xu et al. (2003) examined relationships between only band reflectance values and some VIs obtained from Landsat TM and found that the TM 3 and the NDVI were strongly related to crown closure ($r=-0.82$ and $r=0.83$), respectively.

In the same study, NDVI, SR, NDVISQ and NDVICUB were better correlated with crown closure ($r=0.83$, $r=0.78$, $r=0.85$ and $r=0.85$, respectively). Falkowski et al. (2005) used ASTER satellite image to estimate crown closure in Moscow mountain and achieved a strong positive relationship ($r=-0.84$ for green band), ($r=-0.86$ for red band), and a low negative ($r=-0.29$ for NIR band) and a strong relationship ($r=0.83$ for NDVI), ($r=0.87$ for GRVI) and ($r=0.80$ for SR). He found that use of VIs incorporating green red vegetation index (GRVI) only or in combination with VIs incorporating near-infrared wavelengths (NDVI) showed the strongest relationships ($r=0.80$ and $r=0.83$), respectively. Zeng et al. (2008) used the MODIS data. They found that NDVI showed the highest correlation with the crown closure in the three Gorges region of China for both 2002 ($r=0.6$) and 2004 ($r=0.5$).

A multiple regression model using TM2 and TM4 as independent variables was selected as the best predictor of crown closure with the parameters such as adjusted $R^2=0.529$, $S_{y.x}=0.02716$, bias=4.0539, bias%=6.1006, RMSE=0.0271 and RMSE%=4.0782. The stand crown closure model with VIs were developed by SAVI, ND32 and ND57 as independent variables, and the model performance was calculated and adjusted with $R^2=0.757$, $S_{y.x}=0.01681$, bias=3.9307, bias%=5.9468, RMSE=0.0167 and RMSE%=2.5304. Kahrman et al. (2014) studied the relationship between the crown closure and individual band reflectance values and VIs obtained from Landsat TM satellite images. The model that used TM 1, TM 3 and TM 4 as

independent variables had an R^2 of 0.610 and the other model used the SR and DVI as independent variables had an R^2 of 0.674. Regarding this, Falkowski et al. (2005) compared the regression models for each response variable for crown closure. Green and red band reflectance values showed a strong relationship for crown closure ($R^2=0.71$, $R^2=0.75$), respectively.

The relationship between NIR band values and crown closure was low ($R^2=0.08$). In the same study, the model with the green red vegetation index (GRVI) and NDVI as predictors of crown closure obtained the highest relationship ($R^2=0.77$). Xu et al. (2003) found that regression model with TM 4, TM3 and TM2 as independent variables could better predict crown closure ($R^2=0.80$). Berberoglu et al. (2009) found that Envisat MERIS data with 13 independent waveband variables were related to crown closure ($R^2=0.43$). Chiao (1996) indicated that multiple regression analysis with TM1, TM2 and TM3 as independent variables could better predict crown closure ($R^2=0.90$), with XS1, XS2 and XS3 (SPOT HRV satellite image) as independent variables could predict crown closure ($R^2=0.83$), with MSS₅, MSS₈ and MSS₉ (multi-spectral scanner) as independent variables could moderately estimate crown closure ($R^2=0.53$).

The same study showed that multiple regression analysis with NDVI and DVI (multi-spectral scanner) and, NDVI and ND42 (Landsat TM) as independent variables could predict stand crown closure ($R^2=0.82$, $R^2=0.43$), respectively. The statistical models predicting crown closure from remote sensing data were based on regression models developed by using sample plots located at study area. Therefore, these regression models are statistically valid for the study area may not be applicable to different forest areas. The models developed as part of this study were used to generate crown closure maps (Figs. 4-5). Stand crown closure estimated by both Landsat TM reflectance values and VIs using the models are plotted against these observed forest variables (Fig. 6). Furthermore, polygon themes obtained from the VIs (Fig. 4) and the spectral reflectance values (Fig. 5) were overlaid into each other and areas that are spatially in the same (Fig. 4) or different classes (Fig. 5) were determined using ArcGIS 9.3 to analyze the spatial structure of stand crown closure. Spatial analysis indicated that spatial accuracy of crown closure was 52.5% -the area having the same spatial configuration in the models developed both with VIs and spectral reflectance values.

The models obtained from spectral reflectance values and VIs can be used to determine crown closure in similar forest ecosystems within the study region. The use of high resolution satellite images to determine the crown closure in larger areas is not economical due to higher cost of high resolution satellite images.

Therefore, low-resolution images (i.e., Landsat) should be used and models developed to

determine the crown closure in small areas instead of high-resolution images (i.e., QuickBird and IKONOS). When the models obtained from these areas are evaluated together with low-resolution satellite images, the results can be applied for large areas in similar forest ecosystems. So, the use of satellite images in conducting field inventory necessary for the preparation of forest management plans will significantly reduce the costs of the field inventory in Turkish forestry.

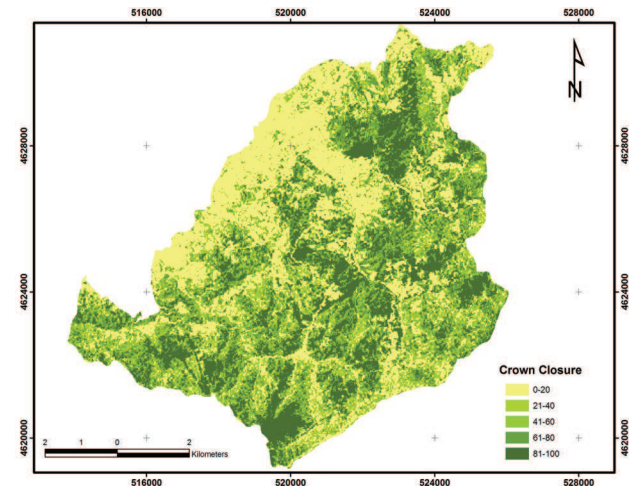


Fig. 4. Stand crown closure (%) estimates generated from Vis

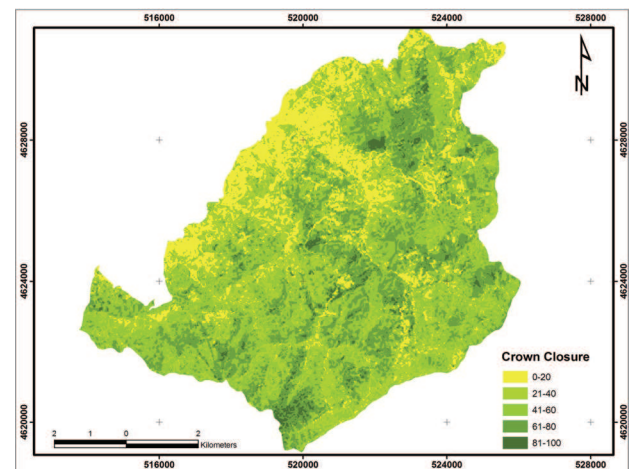


Fig. 5. Stand crown closure (%) estimates generated from Landsat TM spectral reflectance values

6. Conclusions

This study investigated the relationship between reflectance values recorded as well as VIs calculated by Landsat TM sensor and crown closures, using Pearson correlation and multivariate regression analyses. Utilizing empirical relationships between Landsat TM satellite imagery and crown closure helped develop stand crown closure map successfully.

The analysis of crown closure maps indicated that significant improvement has been accomplished through the use of VIs over single bands.

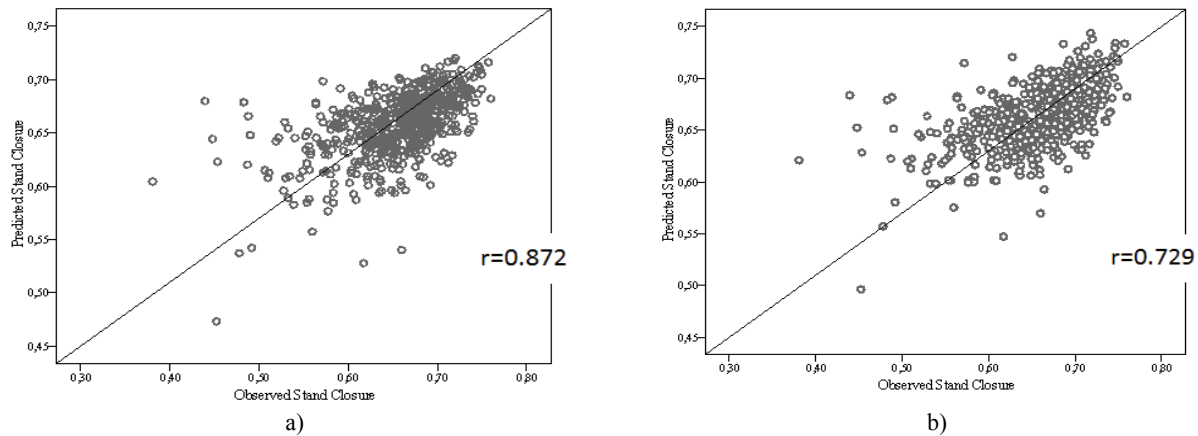


Fig. 6. Comparison between the observed and predicted crown closure by regression models based on VIs (a) and the spectral reflectance values, TM 1-5 and TM 7 (b)

The results imply that forest managers could use Landsat TM data for better estimation of crown closures and such information would also be beneficial for generating maps necessary in developing forest management plans.

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EVALUATION AND ABATEMENT OF ENVIRONMENTAL NOISE. A CASE STUDY FOR DISTRICT HEATING PLANT PLACED IN A RESIDENTIAL AREA OF BRASOV – ROMANIA

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Abstract

In order to reduce public annoyance produced by the noise generated from a District Heating Plant (DHP) upon an urban residential area, a noise assessment was performed. The paper illustrates the evaluation of noise envelope around the DHP, considered as an overall source made of six distinct sound sources. As receptors, there were considered five points on the facades of the closest residential blocks. The specific feature of the research work was the configuration of the area having the DHP in the middle of a block-of-flats district. The very short distances between the DHP building and the neighboring residential blocks lead to the occurrence of reflected sound waves. It was analytically determined the contribution of the noise reflected from block facades to the overall noise upon receptors, focusing on significant weight of reflected noise; the assessment allowed to select noise abatement paths, being analytically calculated noise levels in several abatement scenarios aimed to meet the standards prescribed by European and Romanian statutory bodies.

Key words: district heating plant, environmental noise, noise limits, reflected sound

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1. Introduction

The paper deals with a demand of noise abatement in a district of Brasov, a Romanian city of 270000 inhabitants. In the 1980s the city had a centralised heating system, with the main plant several miles away from the residential areas. Starting from 1989, the centralised heating system was gradually replaced by district units, smaller, less pollutant and more efficient. The new District Heating Plants (DHP) were built among the existent blocks of flats, without considering the noise emissions. Only after joining European Union, Romanian cities started to apply coherent strategies for noise abatement such as noise maps (Petrescu and Borza, 2013; Popescu et al. 2013) which consider also local noise sources in built-up areas.

The European Union stated procedures for the assessment of environmental noise (EC Directive, 2002) limiting the noise expressed in equivalent A-weighted sound level (L_{Aeq}) from transportation and industrial sources in the range of 45 – 55 dB(A), emphasizing the effect on human health and well-being (EEA, 2010). The outdoor threshold noise levels in most European countries legislations expressed in equivalent A-weighted sound level (L_{Aeq}) showed that a moderately annoyance of population will require L_{Aeq} smaller than 50 dB(A). A more serious annoyance is produced if L_{Aeq} exceeds 55 dB(A) during daytime and 45 dB(A) during night time (Gottlob, 1995). The threshold values admitted by Romanian authorities are quite more severe (RHMO, 1997), for residential areas being 50 dB(A) during daytime and 40 dB(A) during night time.

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The paper originates from a technical study which assessed and designed the noise abatement solutions.

As the DHP is surrounded by high block of flats, very closely situated, the weight of reflected noise from overall noise is significant. As a consequence, it cannot be done an accurate selection of noise abatement paths without a prior assessment of reflected noise.

The paper describes the configuration of the area and the sources of noise (section 2), the procedure of noise measurement at sources and at receptors (section 3), analysis of noise paths (section 4), scenarios to abate the noise (section 5) and conclusions (section 6).

2. The noise sources

The DHP consists of a combined heat and power unit (CHPU) based on natural gas internal combustion engine (rated thermal power of 2.48 MWt and rated electric power of 2.674 MWe) and a natural gas hot water boiler of 10 Gcal/h, enclosed in two separate rooms in the same building, in continuous operation. The CHPU is compact, the engine and generator being coupled by flanges, having an elastic suspension which isolates the vibrations of the group. The main noise sources within DHP are the pumps, fans, compressors, air intakes, exhaust gas mufflers, ventilation units, all being situated inside the building with the exception of the engine cooling system which is placed outside the building. In the interior, the noise exposure of the workers is evaluated at 90 dB(A), value which can affect their behavior. The configuration of the area is described in Table 1, considering as reference the DHP building. A general view of DHP and surrounding residential flats can be seen in Fig. 1.

In order to determine the acoustic levels in several representative points chosen for noise analysis, it must be considered the direct sound from the sources but also the reflected sound from the obstacles found on the propagation path, being very important the accuracy in sources positioning and obstacles dimensioning (Barron, 2002; Silva et al., 2014; Tomozei et al., 2014; UFC, 1995). The contribution of a noise source to the overall noise level at receptor in imission point is influenced by: source acoustic power and spectrum, source–receptor distance, obstacles presence and position, reflection angle, height against the ground, local meteorological data and durations. In order to evaluate thoroughly

which are the causes of annoyance people declare, further accurate investigations were required in order to define several noise abatement strategies. The analysis of DHP noise envelope lead to the conclusion that noise sources which can be identified also in Fig. 2, as it follows: S1–cooling system of CHPU, situated on the top of the building, S2–engine air intake, S3–vent air exhaust, S4– wall with low acoustic treatment, S5–access door to CHPU room, S6–access door to boiler room. As a subjective opinion the DHP building noise due to all independent noise sources appeared to have similar values.

3. Noise measurements and work strategy

The following working procedures were performed:

- identification of the main noise sources which could affect neighborhood;
- in situ measurement of the sound pressure level of the sources;
- measurement of noise level in representative points, chosen by prediction (close to flats and windows);
- positioning in cartesian coordinates (x, y, z) the noise sources, reflecting and absorbing surfaces from dwelt area (buildings, obstacles, ground bumps);
- calculation of imission noise levels in relevant points;
- simulation of separate operation of each source and evaluation of its contribution to overall noise level in representative points, before and after the implementation of a noise abatement method;
- comparison of the noise levels to legal threshold values.

The noise levels in representative points were calculated according to international standard (ISO 9613–2, 2006). The main indicator is equivalent continuous A–weighted sound pressure level being considered the physical effects on the attenuation of the geometrical divergence, atmospheric absorbtion, ground effect, surface reflection and obstacle screening.

The calculation of noise indicators were carried out for the situation when the sound propagates in wind direction within an angle of $\pm 45^\circ$ of the direction connecting the centre of the dominant sound source and the centre of the specified receiver region, with the wind blowing from source to receiver.

Table 1. The layout of DHP building

<i>Orientation towards DHP</i>	<i>Obstacle (block facade)</i>	<i>Distance to DHP, [m]</i>
South	A – Block P+4 (5 storey)	19.5
West	B – Block P+4 (5storey)	31.8
North	C – Block P+9 (10 storey)	10.8
East	D – Block P+9 (10storey)	52.0

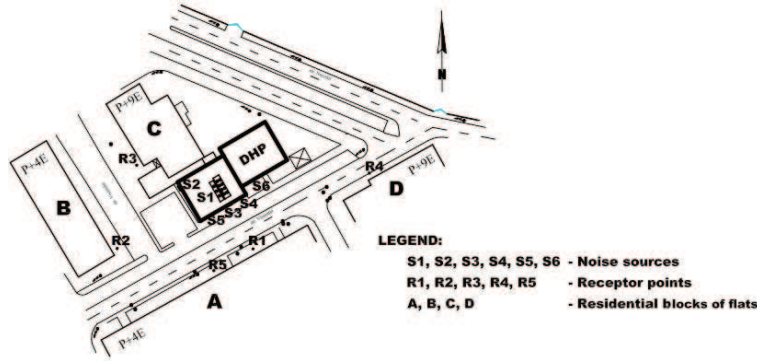


Fig. 1. General view of DHP and residential flats

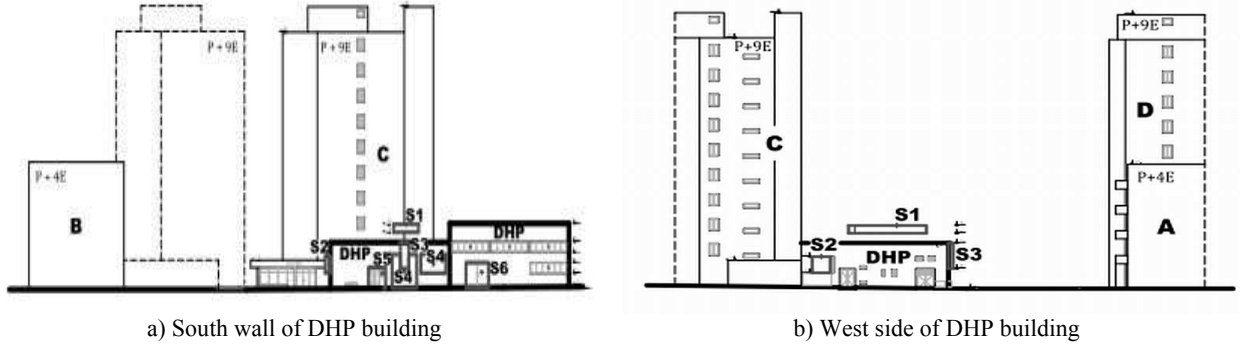


Fig. 2. Noise sources

The equivalent continuous downwind octave-band sound pressure level at a receiver location $L_{JT}(DW)$, was calculated for each point source and its image sources from Eq. (1):

$$L_{JT}(DW) = L_w + D_c - A \text{ [dB]} \quad (1)$$

where L_w – is the octave-band sound power level, in decibels, produced by the point sound source relative to a reference sound power of one picowatt (1 pW); D_c – is the directivity correction, in decibels, that describes the extent by which the equivalent continuous sound pressure level from the point sound source deviates in a specified direction from the level of an omnidirectional point sound source producing sound power level L_w ; A – is the octave-band attenuation, in decibels, that occurs during propagation from the point sound source to the receiver.

The attenuation term A in Eq. (1) is given by Eq. (2):

$$A = A_{div} + A_{atm} + A_{gr} + A_{bar} + A_{misc} \text{ [dB]} \quad (2)$$

where A_{div} – attenuation due to geometrical divergence; A_{atm} – attenuation due to atmospheric absorption; A_{gr} – attenuation due to the ground effect; A_{bar} – attenuation due to a barrier; A_{misc} – attenuation due to miscellaneous other effects.

The equivalent continuous A-weighted downwind sound pressure level is calculated by summing the contributing time-mean-square sound pressures, for each point source and its image sources, according to Eq. (3):

$$L_{AT}(DW) = 10 \log \left\{ \sum_{i=1}^n \left[10^{0.1 \cdot L_{JT}(i)} \right] \right\} \text{ [dB]} \quad (3)$$

where n is the number of contributions i (sources and paths).

As the working program of industrial activities generating noise is the same around a day (24 hours), there were no significant noise variations, and therefore the authors did not compute the L_{Aeq} sound level for 24 hours.

The sound acquisition and analysis was integrated in a National Instruments (NI) Virtual Instrumentation (VI) system, with a USB-DAQ data acquisition module (connected to the sono-meter output), driven by NI-DAQmx middleware and running the “Sound & Vibration” toolkit in the NI LabVIEW software environment. The main blocks of the VI diagrams were „SI CONFIG” (Sound Input Configuration – to set format, sampling rate as divisions of the standard 44100 Hz value, number of bits/sample and the size of the buffer memory) and session controls („SI START”, „SI READ” – from the USB-DAQ – and „SI CLEAR”). Sound post processing employed windowing and audiometric level assessment; the data acquisition resolution was 14 bits / sample.

The noise measurements were performed with a memory integrator sound level meter type SOLO-SLM: range 30 – 137 dB (class 1), A-, B- and C-weightings across the frequency and Lin, accuracy IEC 804 and IEC 651 class 1, (BAV) for a detachable microphone, calibrator, weather station WS1070. The measurements were performed in summer time. The ambient temperature was considered in calculations having a mean value of 20°C; the wind speed indicated by the weather station during noise measurements was 0.0 m/s, thus eliminating the meteorological corrections.

The sound power levels (L_{Aw}) expressed in A-weighted decibels of the six noise sources were measured in Table 2. The sound power levels L_{Aw} were determined according to standard based on measured sound pressure levels, L_{Aeq} (ISO 3744, 1997). The five receptor points as described in figure 1 were set on the block facades with the microphone position situated at 1.5 m above the ground and at 2.0 m from the facade of the closest block of flats (figure 1): R1 – on the facade of block A, R2 – on the facade of block B, R3 – on the facade of block C, R4 – on the facade of block D, R5 – on the facade of block A. The highest value was on the air intake source and the smallest was on the access door to CHPU.

There were chosen two points on the facade of block A, because R1 is the closest to DHP and R5 receives the direct sound of all analyzed sources, being the most exposed point. To compare the estimative calculations there were performed measurements of sound level equivalent level, L_{Aeq} , in dB(A), during daytime in selected points (R) as presented in Table 3. The calculated values are closed to measured ones and measured background noise is higher than threshold limits (50 dBA) showing that there are other noise sources which contribute to the background noise, in this case the road transportation (Mak and Leung, 2013).

4. Analysis of the sound propagation paths

The noise envelope generated by DHP produces reflections on the facades of neighboring blocks of flats. Immission points pick up direct and reflected sound, their overall level being a logarithmic sum of both sounds. The analysis of the sound propagation paths (direct and reflected wave) allowed the finding of the weight of each source in the overall noise level of immission points leading further to the selection of abatement method.

For example, the source S1 (cooling system of CHPU) is situated on the top of the building, at 7.25 m above the ground, the visualization of the direct and reflected sound waves being illustrated in Fig. 3. For each of the sources S2 – S6 is analyzed its position among obstacles and directions of sound waves are evaluated accordingly. The analysis of the sound propagation paths uses the image source method; the first sound reflection was considered as its contribution is the highest.

So, it can be observed the following:

- In front of block A, point R1 (Fig. 4a), the main sources affecting directly the noise level are S1, S3 and S4;

- For the front of block A, in point R5 (Fig. 4b), all the sources contribute directly to the noise level:

- in the front of block B, in point R2 (Fig. 4c), the main sources affecting directly the noise level are S1, S2 and S3;

- in the front of block C, in point R3 (Fig. 4d), the noise level is produced only by reflections from sources S1, S2 and S3, the highest contribution belonging to source S2;

- In the front of block D, in point R4 (Fig. 4e), the noise level is produced only by direct noise propagated from sources S1, S3, S4, S5 and S6.

In Table 4 is presented the increase of the overall noise level, $L_{AT}(DW)$, due to the reflected noise $L_{AT-RS}(DW)$, in each receptor point.

As a consequence, the noise level produced by reflections is rather high, close to the value of direct noise; so, an abatement method is to divert the reflections in other directions to avoid the surface of blocks and living area.

The analysis of the contribution of direct and indirect noise (Fig. 4) for each representative point leads to the identification of the sources which influences directly the immission noise (reflections) and the weight of them in the overall noise. Those observations were very useful in the selection of abatement methods; it could be estimated the minimum required abatement of each source; for reflections cancellation it was considered the redirecting of the sound waves towards directions which avoid the increase of noise level in front of block of flats.

The noise levels in receptor points were calculated in logarithmic summing the direct and reflected noise level (Fig. 5). The highest noise levels were in R5, R1 and R2 points, in decreasing order.

Table 2. Sound power levels, L_{Aw} , in dB(A)

Noise source	Position	L_{Aw}
S1 – Cooling system CHPU	Roof	85.50
S2 – Air intake	West side	88.27
S3 – Air exhaust	South side	85.66
S4 – CHPU wall	South side	84.09
S5 – Access door to CHPU	South side	77.84
S6 – Access door to boiler	South side	81.67

Table 3. Sound pressure equivalent level, L_{Aeq} , in dB(A)

	<i>Measured</i>	<i>Calculated</i>	<i>Background</i>
R1	59.7	59.4	— *)
R2	57.5	57.4	54.1
R3	57.4	53.5	50.4
R4	52.6	50.4	— *)
R5	59.1	60.6	53.8

*) Not measured.

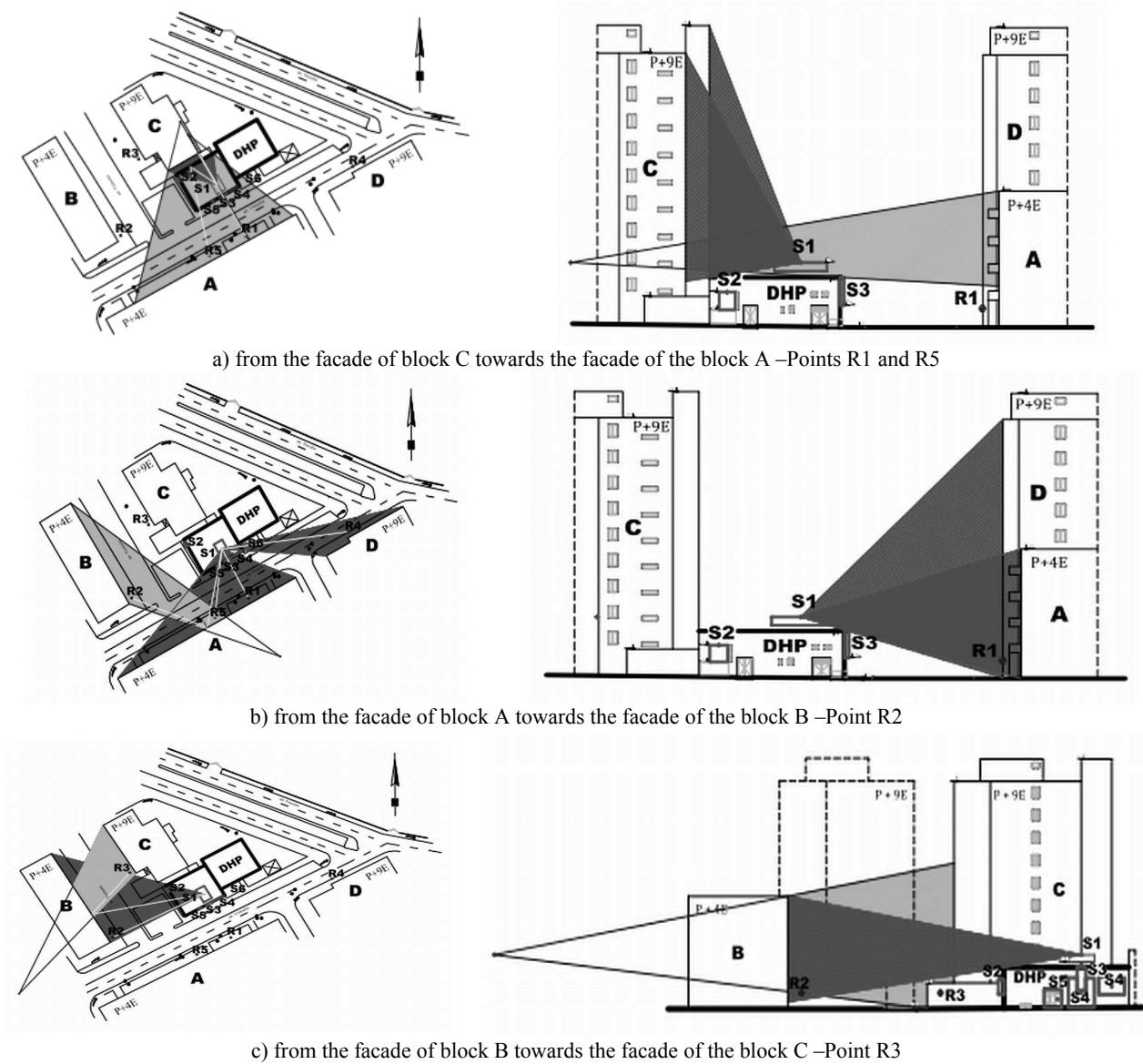


Fig. 3. Source S1 reflections (S – Noise sources, R – Receptor points, A, B, C, D – Blocks of flats, black line – direct sound, grey line – reflected sound)

Table 4. Contribution of the reflected noise to the overall noise level

	$L_{AT}(DW)$	$L_{AT_RS}(DW)$	<i>Contribution of the reflected noise to the overall noise level</i>
	dB(A)	dB(A)	dB(A)
R1	59.44	53.10	1.15
R2	57.42	48.29	1.33
R3	53.54	53.54	53.54
R4	50.42	0.00	0.00
R5	60.64	56.65	2.21

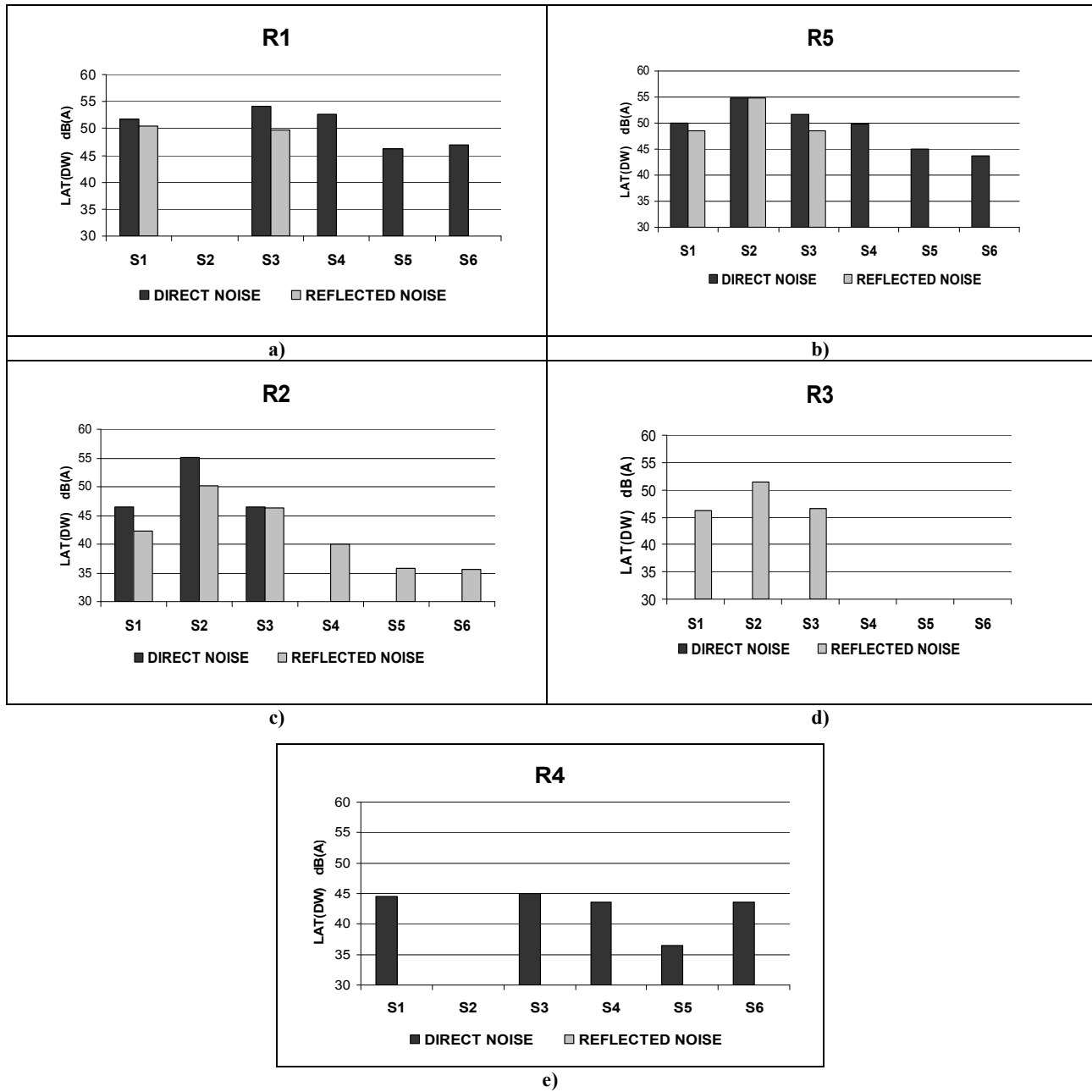


Fig. 4. Contribution of direct and indirect noise (reflections) to the overall noise

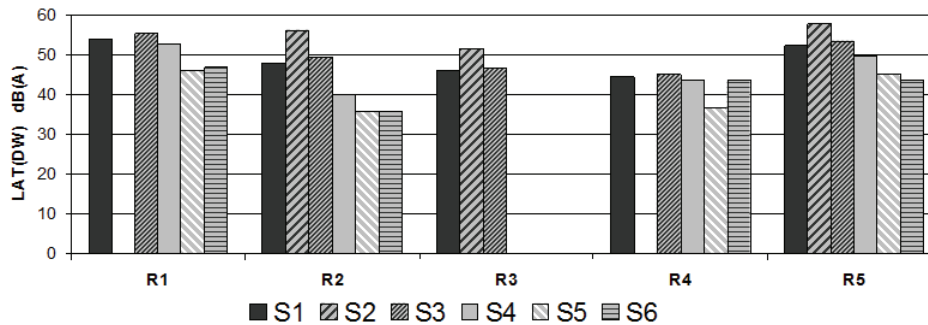


Fig. 5. Noise levels of main sources in receptor points

The sources with the highest contribution to noise level are S1, S2, S3 and S4. In point R1, as opposite to point R5, the contribution of the source S2 is zero.

The selection of two points was helpful to analyze the S2 contribution from the facade of block A, the most affected block by the DHP noise.

5. Noise abatement scenarios

In order to reduce noise levels there were analysed several measures of noise attenuation such as: mounting phono-isolator panels plated with phono-absorbent materials on DHP outdoor walls, fitting of active noise silencers on the exhaust gas duct, mounting phono-absorbent layers on the indoor of DHP walls and designing a lobby with a second door for the access to the boiler room.

The first applied measure was the building of an acoustic barrier on the top of the DHP building around the cooling system (Bies and Hansen, 2003; Hua and Duhamel, 1994; Osman, 2003). In order to get a cone of acoustic shadow to cover a lock facades (Fig. 6), the screen will be placed at maximum 2 m from source S1, the screen height being of minimum 4 m, and the vertical difference between cooling system and screen to be minimum 1.85 m. The mounting of the acoustic barrier close to source S1 is very effective for noise abatement to receptors R1 and R5. By placing the acoustic barrier, the reflected wave will be diverted in such a way not to reach the

facade of block A. To the facade will reach only the wave reflected by the edge of the screen. It was analytically calculated the noise reduction which will be obtained by mounting the acoustic barrier to S1.

Comparing the sound pressure levels in receptor points before and after mounting the acoustic barrier, it can be observed a significant noise reduction, as illustrated in Table 5.

Another suggested measure was to mount at the entrance of intake and exhaust ducts active silencers, as described in Fig. 7. For noise abatement the intake and exhaust duct of the silencers were oriented to a convenient direction. The potential sound pressure levels intended to be reached through the application of all measures of noise abatement are depicted in Fig. 8.

The weight of each source in the overall noise, in receptor points after applying abatement measures will be less than the limit of 40 dB(A) which is marked in figure with an horizontal line, thus allowing to meet the noise thresholds. Sound pressure levels which are estimated to be obtained in receptor points are illustrated in Fig. 8.

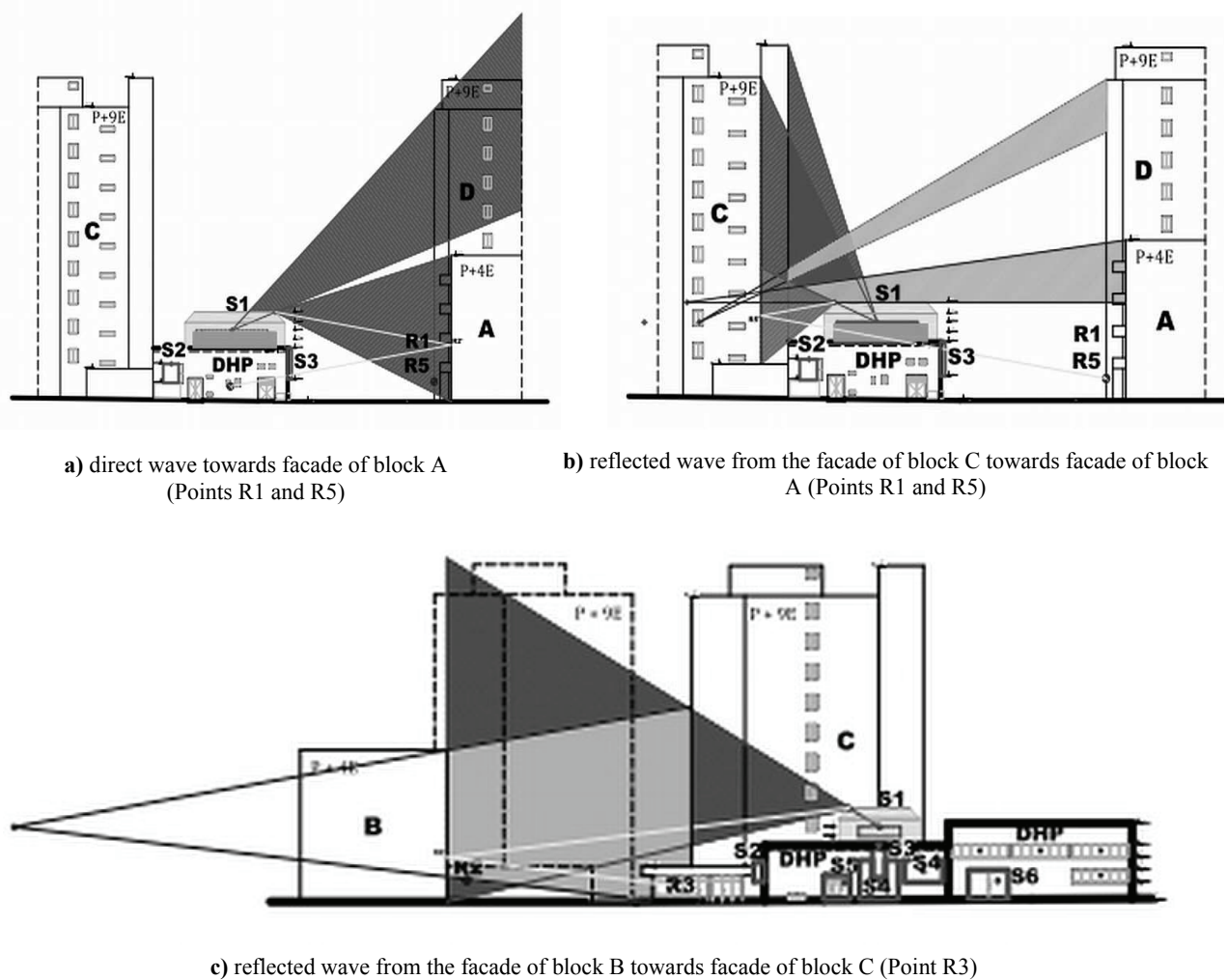


Fig. 6. Noise propagation from source S1 (S – Noise sources, R – Receptor points, A, B, C, D – Blocks of flats, black line – direct sound, grey line – reflected sound)

Table 5. Equivalent continuous downwind sound pressure levels, $L_{AT}(DW)$, in dB(A) at source S1 before and after applying the acoustic barrier

	Noise levels before treatment	Noise levels after treatment
R1	54.1	33.5
R2	48.3	32.8
R3	46.4	31.1
R4	44.5	29.4
R5	52.6	36.4

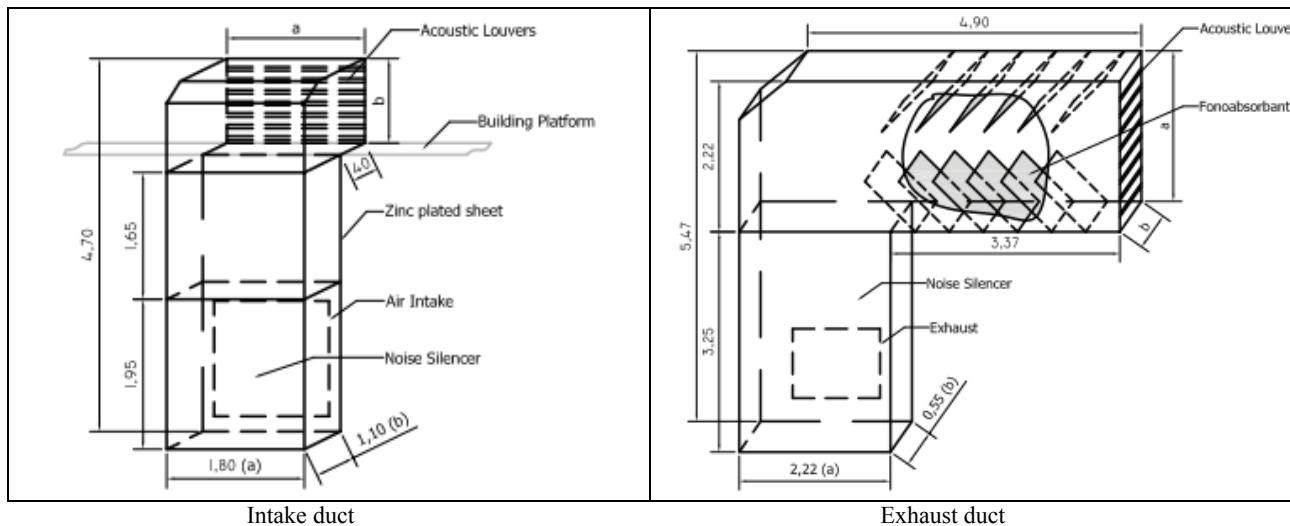


Fig. 7. Noise silencers

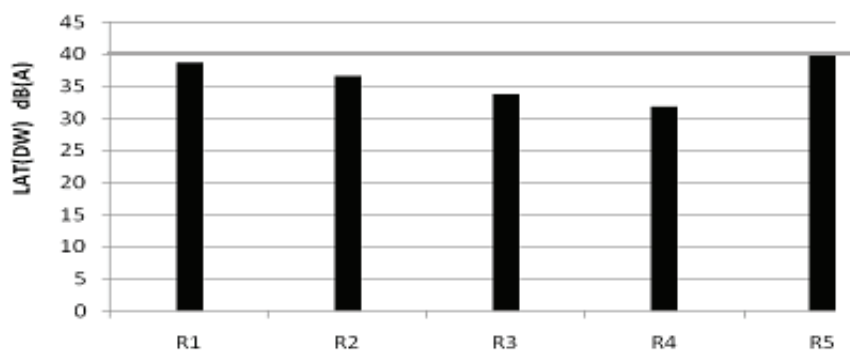


Fig. 8. Estimated sound pressure levels

6. Conclusions

The noise measurements performed in the area of the district heating plant showed that at the level of receptors the values are of 50 – 60 dB(A) either measured or calculated, being exceeded the threshold European values (55 dB(A) during daytime and 45 dB(A) during night time) and Romanian standards (50 dB(A) during daytime and 40 dB(A) during night time). The particularity of the case study is done by the presence of very intense noise sources in the middle of an urban area; the reflections made the analysis of propagation paths more difficult, contributing with significant values to immision noise – as illustrated in Fig. 4: in point R1 – 1.15 dB(A), in point R5 – 2.21 dB(A), in point R2 – 1.33 dB(A) and in point R3 – all noise is reflected noise.

Analyzing the reflections contribution lead to the selection of acoustic barrier as the solution of noise attenuation; investigating the propagation path of reflected noise lead to the accurate dimensions and positions of the acoustic barriers. Abatement scenarios were detailed allowing the simulation and prediction of the effects acquired by noise attenuation at source. By placing a acoustic barrier, with an appropriate height, to S1, the noise attenuation is high leading to the complying of standard values, as can be seen in Table 5.

Excepting the placement of acoustic barrier which removed a part of reflected waves, the other suggested measures were intended to redirect of the reflected noise in opposite directions to block of flats. There were designed active noise silencers on air intake and exhaust, thickening the phono-absorbent

isolator on the walls, designing a lobby with a second door for the access to the boiler room.

The selection of noise abatement paths was based on several criteria such as simplicity, ease of manufacturing and low costs. Redirectioning of acoustic waves in such of manner to reduce reflected waves was one of the simplest and most efficient solutions. As figure 8 illustrates, the applications of abatement methods lead to, analytically estimated, lower sound pressure levels which meet the provisions of noise standard requirements.

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RESEARCH AND TRENDS IN PRODUCT LIFE CYCLE MANAGEMENT IN THE CONTEXT OF SUSTAINABLE DEVELOPMENT

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Abstract

During the creation of a product, the majority of the enterprises still apply a linear approach. This approach has been imposed by the organization way of the company and by the informational flow between the different departments.

In the present time different models of integrated engineering oppose to the sequential organization. These models permit the simultaneity of the activities deploying or at least their partial overlap. The activities overlap can be imagined eliminating first of all the borders between the phases of the product creation stage. This way, when an activity arrives to dispose of enough information, it will have the possibility to start before the end of the previous one.

Early in the design phase it has to be taken into consideration that the recycling activity is deployed on the entire life time of the product, so we'll have recycling in the stage of product development, in the production stage, in the exploitation phase and in the cassation phase. The products will incorporate new designing technologies that take into consideration the recycling process that will be applied to the product after utilization. The paper presents a comparative analysis of the visions belonging to the main industrial trusts concerning the life cycle of the product. In this context it is underlined the personal inspiration upon the life cycle including the analysis of the contributions brought to this interesting subject.

The selection of the research methodology was made based on the research topic, namely products' life cycle and the empirical approach method. The authors' contributions will lead to: thoroughness of knowledge on the new approach method for developing metallic products; pollution mitigation by recycling carried out on life cycle stages; new interpretation of products' dismantling as a quality issue.

Key words: product life cycle management, sustainable development, materials

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1. Introduction

The life cycle of one product, especially an auto product, encloses several important industrial areas of interest such as the petroleum, steel, aluminum, chemicals, synthetic fibers, glass and electronics (Amza, 2006). The automotive industry is the only one which has succeeded to make noteworthy steps in expanding the ecological responsibility of its own products ever since the designing stage and until their removal from usage. The consumption stage of the products represents a

significant source of ecological impact, as in this stage it is used approximately 80-90% of the whole energy, the auto industry is focusing upon this phase. The efficiency standards of the fuel and the standards concerning the emissions are the main reasons for achieving some improvements relating to the ecological performances of the product in the usage period (Kamel, 2009).

The recycling activity must be developed during the whole life spam of the product. Ever since the designing stage there must be taken into consideration the fact that the idea of recycling

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should become a permanent concern for the whole life time of the product. Nowadays we can mention that there is a placed more important accent upon the recycling in the phase of product development, the recycling in the production stage, recycling in the exploitation phase and recycling in the stage of removal from usage (Beju et al., 2006; Corabieru, 2009b).

The analysis of the life cycle of the products can offer to the companies a comprehensible basis for taking the proper decision in applying the improvement measures about diminishing the environmental impacts associated to the produced products (Edquist, 2005). The analysis of the life cycle of the products implies the decision of taking the measures which will allow obtaining the most important ecological and economical benefices as well as the identification of the specific potentials for each phase from the life cycle of the products (Corabieru, 2010).

2. Research methodology

The approach method is clarified as a reflection process in relation to the epistemological and methodological requirements. This way, a thorough scientific research and a presentation of the options can be conducted on scientific criteria. Under Table 1 it is presented the systematic method for selecting the methodology and making epistemological choices on each stage of the endeavour, correlated to the type of necessary and achieved research.

The research methodology allows the analysis of various visions on product's life cycle. The comparative analysis is the root of the holistic assembly of a new vision developed by the authors. The different advantages of each individual vision are taken into account (Corabieru et al., 2014).

3. Current vision of the product life cycle

During the '90's there was developed the concept of CIM (Computer Integrated Manufacturing) which presupposes the organization

of a company upon the services attached to the life cycle of the product, ensuring the computer means and their connection to a network.

The designing and manufacture stage of the life cycle remains a linear and sequential approach imposed by the organization way of the company and by the information flow between the different services. This vision is a structure taking into account the chronology of all activities which are prolonging the time of the manufacturing cycle (Ciobanu et al., 2006). The used methodology is the integrated engineering which allows the integrated and simultaneous conception of the products and of the manufacturing processes together with the associated maintenance activities.

The integrated engineering is ensuring the consideration of all phases belonging to the life cycle of the product, integrating all issued concerning the quality, the deadlines, the costs and the user's demands. The implementation of the integrated engineering methodology had permitted the simultaneity of activity development and of all phases associated to the product creation steps and manufacture (Ojasalo, 2008).

4. Vision main industrial concerns of the product life cycle

The purpose of the improvement of the products development is to concentrate the human imagination such that the result of the designing processes represents a connections system acceptable from the point of view of utilization and efficiency (Corabieru, 2009a; Corabieru et al., 2009). Initiatives and projects that have in view the improvement of the products development at global level are multiple both in scientific and industrial environment (Per Sundström and Zika-Viktorsson, 2009).

All are aimed at processes of improvement of the products that have to be more flexible, more adaptable and more dynamic, at a small price. On a global scale, the accent is put on the digital development in order to shorten the project loops and attentive forming of the subordinated organizational culture and structure.

Table 1. The summary of epistemological and methodological choices

	<i>Selected solution</i>
1. Research planning	
Endeavours	Case studies. Endeavours based on the approach empiricism.
Tools	Operational concepts that outline basic criteria. These criteria allow highlighting the company's performance in relation to products' life cycle.
2. Epistemological perspective and research scope	
Epistemological perspective	Constructivism. Positivism (epistemological perspective adapted to each type of product).
Research scope	Description. Explanation. The particular scope of each stage is outlines.
3. Methodology	
Appropriated epistemological distinction	Emic. Etic. The understanding of particular situations is aimed at.
Method	A mixture between the qualitative and quantitative method is obtained.
Data collection	Observation. Analysis of statistical data.
4. Implications	
Implications	The aim is complex research of product's life cycle. The aim is building of a support to facilitate decision-making.

In Fig. 1 the new way of approach of the products development is schematically shown (Johnston and Bate, 2003 Velicu et al., 2009).

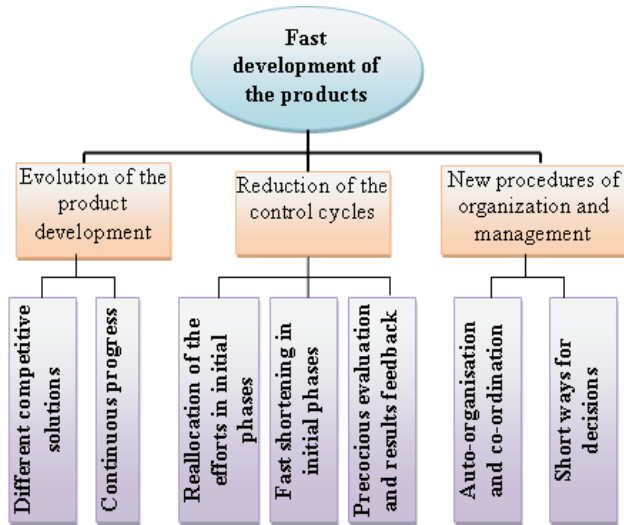


Fig. 1. New way to the fast development of the products

One of the studies achieved by an automotive company (C1) shows that following the use of the Opera software the best selections of materials and great facilities of disassembling have been obtained. It is a soft that suggests a recycling rate of 95 % by using the plastics (Corabieru, 2009b; Popovic and Milenkovic, 2009). Using the Opera software, the recycle of propylene at the vehicle C1 should reach a rate of 50 kg per vehicle in 2016, as illustrated in the Fig. 2.

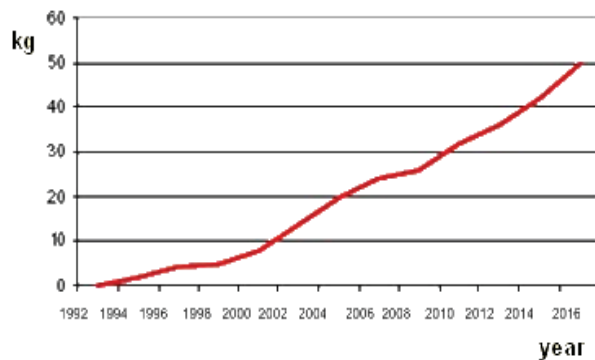


Fig. 2. Evolution of propylene recycling on the vehicles C1 for the period 1992-2016

The internal norms and the recommendations regarding the choice of the materials in terms of eco-design for the norms C1 are illustrated in Fig. 3 (Norme Conception en Vue du Recyclage 00-10-060/2002). Evolution of plastics in comparison with others used in Europe is shown in Fig. 4. As per the Federation of the Producers of Plastics the improvement of the participation quota of these materials is much faster than of the aluminium, opening this way great perspective in this process.

C1 Company focuses on two main directions in the products development:

- replacement of the metallic materials that leads to the decrease of the product weight having a direct effect on the reduction of the fuel consumption and implicitly the reduction of the pollutant emissions quantities;
- increase of the capacity of products recycling.

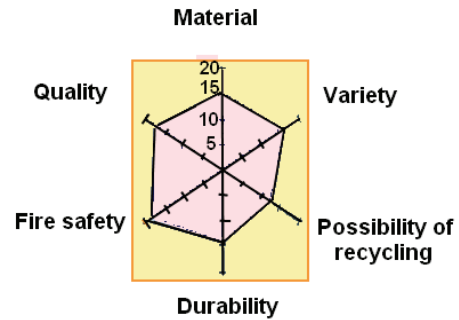


Fig. 3. Criteria and constraints of materials selection for C1

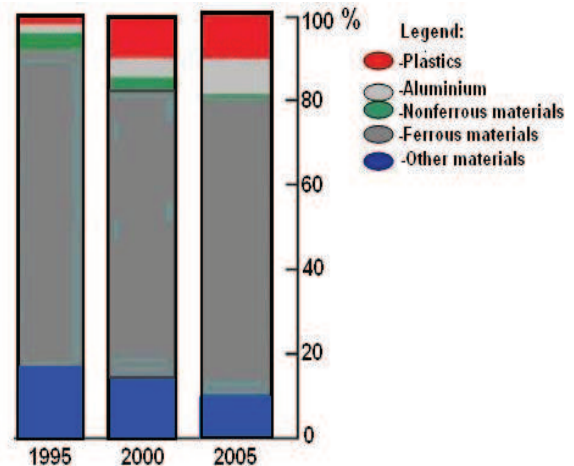


Fig. 4. Evolution of the materials used in the manufacture of products for vehicles conforming to C1

Another automotive company (C2) approaches the product development by the prism of the design oriented towards the recycling that increases the product efficiency. C2 recycling initiatives have as purpose the reduction of the waste by specific measures during the vehicles production and the recuperation of these ones at the end of the life cycle, conserving this way the valuable raw materials and the energetic resources.

The recycling strategy of C2 Company into the context of the product development is an element of the integrated responsibility by respect to the product (Fig. 5) and it is based on two fundamental elements:

- design oriented towards the products recycling;
- development and utilization of materials recycling in closed loop, in the vehicle production (Fig. 6).

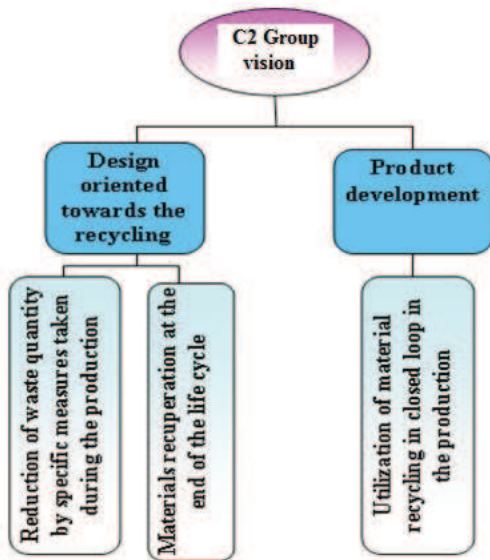


Fig. 5. Vision of C2 – integrated responsibility by respect to the product

To take into consideration these objectives still in the phase of product development, a global team of experts created a specification for the design oriented towards the recycling, compulsory into the framework of the entire group C2 in the world.

The objective of this specification is to assist both the engineers of C2 and the suppliers in developing vehicles and component parts oriented towards the recycling. Further, this specification helps the researchers to study the parts, component parts and vehicles from the point of view of the recycling capacity and recovery and to determine the product specific features (Velicu et al., 2009, Zait et al., 2008). Utilization of the recycled materials represents a tradition of the group C2, since they used more than 30.000 tons of recycled materials in 2001 for the production of new vehicles. Until now more than 70 types of recycled plastics have been specified and launched in production.

The recycled materials are preferred to the new materials if they can be produced at lower costs and in the same time they fulfill all the technical specifications. Anyway, the specialists in recycling don't accept compromises regarding the tactile or optical characteristics, the strength or thermal resistance or other performance characteristics.

Due to the high quality of the recycled materials they are utilized not only for the hidden parts, but also in visible places. The aim is to increase continuously the recycled plastics quantity during the life time of the pattern, up to 20% of the entire plastic content.

The C3 Group approaches product development by emphasizing three elements: the analysis of the recycling product; improvement of service interventions; processing of discarded items by a specific process. The products' life cycle is approached globally. Through this approach method, the C3 Group obtains an environmental recovery of the parts higher than 80%. The recycled parts are traded with full warranty as "original spare part".

C4 Concern focuses on recycling early stage product design targeting over 10 years a 95% recyclable. In Fig. 8 is presented C4 Group's vision of the product life cycle. Existence of dismantling manuals for each product in conjunction with restoring worn parts led to the use of the system with full warranty replacement of over 2000 components.

5. Extended product life cycle vision

The comparative analysis of the perspectives on product's life cycle leads to the necessity of a more complex treatment of life cycle seen holistically in relation to the environment. Based on the comparative analysis, authors draw their own vision on products' life cycle. This new vision carries out an extensive analysis on life cycle with an integrated responsibility in relation to the product and recycling closed-loop materials.

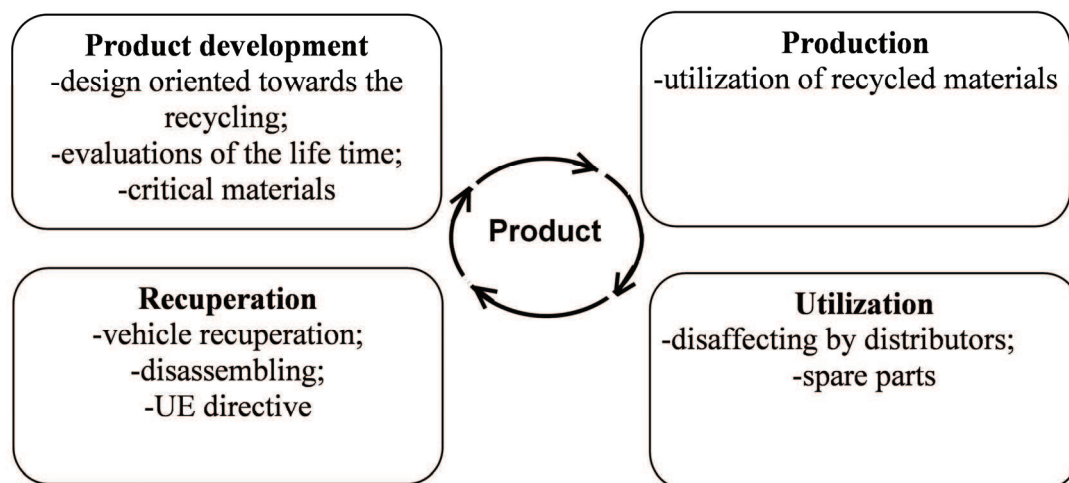


Fig. 6. Development and utilization of materials recycling in closed loop

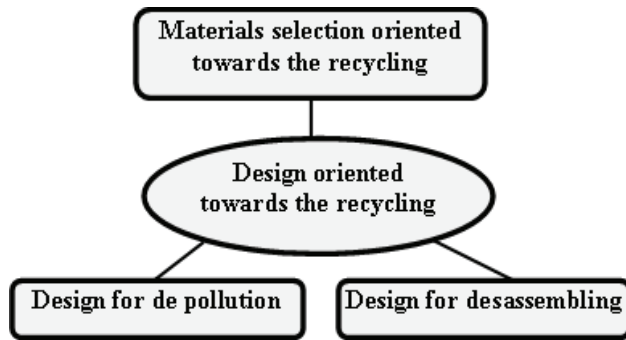


Fig. 7. Elements of designing for recycling

The vision upon extended life cycle is concentrated on the following features:

- an extended life cycle after the removal from usage of the product;
- integrated responsibility towards the product;
- recycling the materials in closed loop in the manufacturing process.

The life cycle of the product is regarded as a whole made of four main trails in direct or indirect connection with the environment. The four main tracks are the following:

- the product's conception;
- the product's manufacture;
- the use of the product;
- the product's removal from usage.

The connecting channels between the trajectories are the direct ones from one trail to another in the order of the normal and the inter-trajectory succession. The main inter-trajectory connecting channels are the so-called inter-trajectory ecological channels as follows: I - Direct re-cycling; II - Commercialization with complete guarantee under the name „original spare part“;

III - Commercialization of second-hand spare parts; IV - Re-manufacturing the reusable components; V - Re-processing the materials; VI - The regeneration of the raw material.

From the closed circuit: environment – product conception – manufacture – usage – removal from usage – environment, we can detach three exterior channels: e1- production of clean fuel using the extracted and collected fluids from the dismembering operation; e2 - definitively moving off and burying slight residues representing 2% of the initial mass of the production; e3 - burning off slight residues in order to recuperate the energy-giving content.

The main trajectory „the product's conception“ is activated and triggered as a result of the disposal resulted from the market analysis in connection with the report supply/offer (Corabieru, 2009b). Since the conception phase the product must take into consideration the European environmental directives. The product's design is segmented upon three stages of development with the following specific particularities:

1. The product's planning – the project theme: decreasing the quantity of waste through specific measures during the production; recuperating the materials at the end of the life cycle;
2. Preliminary projection of the product: diminishing the polluting emissions; the extensive usage of the recycled components; designing the materials' recycling in closed loop production;
3. Execution design and product development: marking the components' materials; checking upon the ecological particularities through the analysis of the recycle process; dismembering manuals for each product.

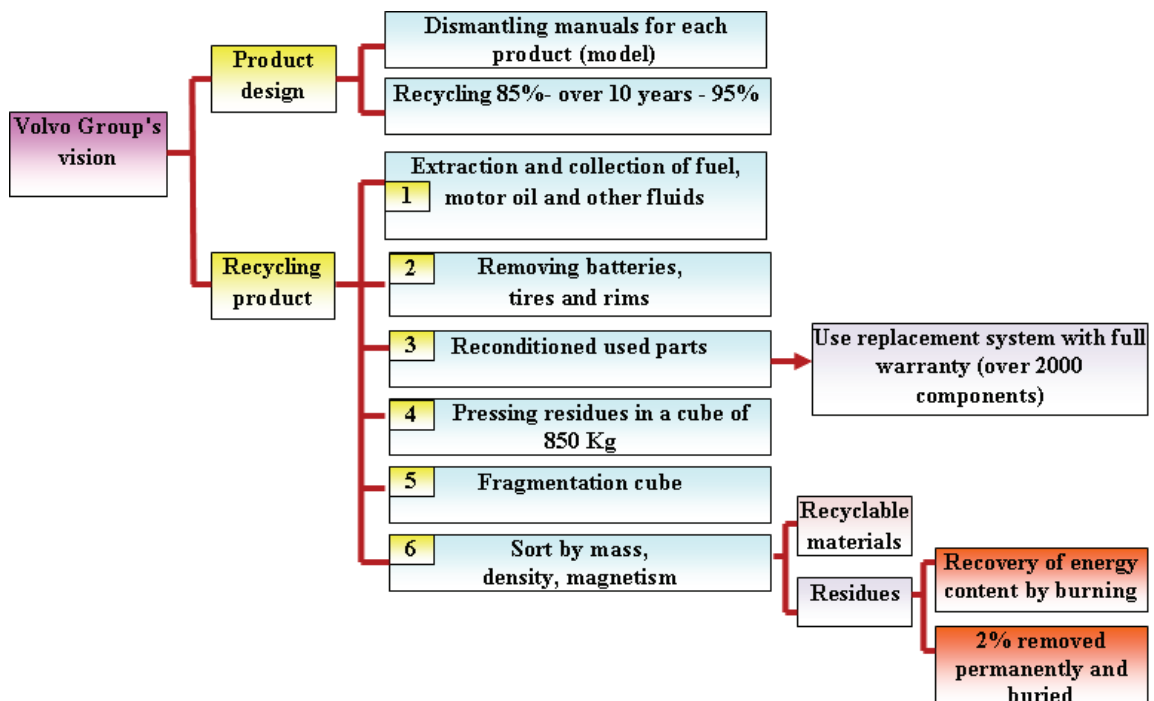


Fig. 8. C4 Group's vision of the product life cycle

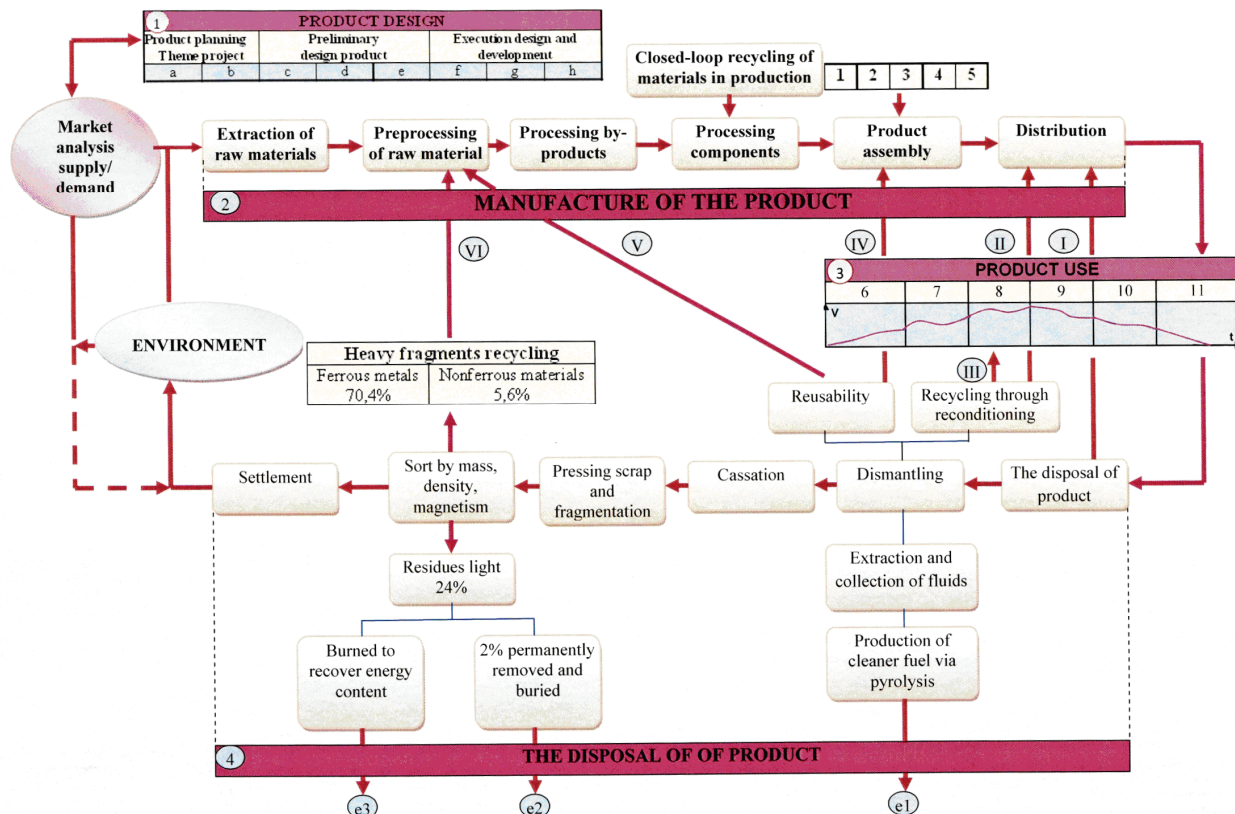


Fig. 9. The extended life span of the product with the integrated responsibility towards the product and recycling the materials in closed loop (Corabieru, 2009b)

Legend: a. decreasing the waste quantity by specific measures during the manufacturing process; b. recuperating the materials at the end of the life cycle; c. diminishing the polluting emissions; d. the extended usage of the recycled components; e. projecting the recycling of the materials in closed loop during their production; f. marking all material's components; g. checking upon the ecological particularities through the analysis of the recycling process; h. manuals of dismembering for each product; 1. components included in the product; 2. personalizing the components; 3. finalizing the summing process; 4. integrating the components – the way and order of assembling procedure; 5. test functioning - evaluation; 6. start; 7. evolution growth: – decreased consume of fuel; 8. stability with turbulences: – improving the interventions in the service; – improving the reliability; 9. maturity: – increasing the life span with economies made to the primary materials; 10. decline; 11. the oldness process: – redrawing the product; I. Direct recycling; II. Commercialization with complete guarantee under the name „original spare part”; III. Commercialization of second-hand spare parts; IV. Re-manufacturing the reusable components; V. Re-processing the materials; VI. Regeneration of the primary materials; e1. the production of clean fuel using the extracted and collected fluids from the dismembering operation; e2. permanently moving off and burying slight residues representing 2% of the initial mass of the product; e3. burning off slight residues in order to recuperate the energy-giving content.

The main trajectory „the product's manufacturing” comprises as main operation the assembling of the product analyzed under the following aspects: components included in the product; personalizing components; finalizing the process and summing; the integration of the components – the assembling way and order; functioning - evaluation test.

The trajectory „the product's usage” is aiming as performance objective to improve the interventions in the service as well as the product's reliability thus enhancing the life span with economies of primary materials. The redrawing of the product is considered to be an important step which had to be done quickly and without unjustified abandonment, in specific collecting processes in specialized centers.

The trajectory „the product's removal from usage” has become one of the most complex, as from here it starts all six main inter-trajectory ecological channels and are detached the three exterior channels.

It is followed the maximization of the recycling process, the material re-processing and the primary material regeneration.

The complex idea of the product's life span is underlining the loop of the main trajectories interconnected through ecological recuperation and recycling channels. The recycling activity is developed throughout the whole product's life, thus we would have:

- re-cycling on the trajectory belonging to the product's manufacturing (using mainly slightly recycling materials). Activity complies with the European Directive no. 99/13/EC on the limitation of emissions of volatile organic compounds. When cleaning surfaces, emission limit value $ELV < 20 \text{ mg C / Nm}^3$, and if metal cover $ELV < 75 \text{ mg C / Nm}^3$. (Corabieru, 2007).

- re-cycling upon the trajectory belonging to the product's usage (planning the costs of detachment, transport, preparing for the re-cycling and treatment for obtaining a re-cycled product considered as new

in conditions of economical efficiency). Activity complies with the European Directive no. 76/464/EEC on reducing discharges of dangerous substances into the aquatic environment of the Community (are reduced discharges of chlorine by-products, are eliminated discharges containing cadmium and mercury);

- re-cycling after the redrawing the product (slight disassembling corroborated with the continuous decrease of the number of components left after the re-cycling process). Activity complies with the European Directive no. 2000/53/EC on used vehicles. In 2015, reuse and recovery of used vehicles will reach at least 95% by an average weight / vehicle (Corabieru, 2007).

- disassembling is made by specialized companies or by the producer and it is configured ever since the conception stage. The material and energetic quantities taken out of the circuit of the main trajectories through the three exterior channels must be slowly reduced as volume, maximizing and enhancing the management of the product's life cycle (Corabieru, 2009b).

6. Conclusions

- The traditional product's life cycle is a sequential one, with a linear development, from the phase of raw material until its removal from usage. The product's recuperation and re-cycling has altered this linear evolution into a cyclical one, embracing a certain degree of product's re-cycling;

- The analysis of the life span is a method where the energy and the consume of raw material, the different types of emissions and other important factors belonging to a specific product are measured, analyzed and totalized along the whole life cycle and from an ecological point of view;

- The management of the product's life cycle belonging to the industrial concerns has as main objective the permanent analysis of the following economical criteria: added value (service, re-usage, re-cycling), time and cost (utilization, performance, efficiency, productivity, the logistic-criteria), flexibility (habit, changeability) and quality.

- Nowadays the improvement of the product's life cycle management has in view the self-organization, the coordination, the short paths for the decisions, reducing the control cycles by re-allowance of the efforts from the initial phases, a rapid shortening of the overlaps, the early evaluation and the results' feedback.

- Research led by authors from drawing broad vision. The extended vision upon the life cycle is concentrated upon the following features: an extended life cycle after the removal from usage of the product; integrated responsibility towards the product; recycling the materials in closed loop in the manufacturing process.

- The life cycle of the product is regarded as a whole made of four main trails in direct or indirect connection with the environment. Recycling

activities comply with the requirements of European Directives no. 99/13/EC and 76/464/EEC and 2000/53/EC.

The extended life span of the product with the integrated responsibility towards the product and recycling the materials in closed loop is contributing to the knowledge development in the field through a complex vision upon the life cycle regarded as holistic in its inter-connection with the environment.

Acknowledgements

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A SIMULATION STUDY ON THE DIESEL ENGINE COMBUSTION PROCESS BASED ON THE FIELD-EFFECT ANALYSIS METHOD OF COMBINED COMBUSTION

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Abstract

Based on the spray mixing field-effect analysis method, this paper has taken into consideration the variation in the distribution of oxygen concentration in the combustion process and has put forward the combined combustion field-effect analysis method. The method is applied to the matching study of a certain kind of diesel engine's combustion chamber with air admission and fuel injection parameters and can also be used to complete the simulation analysis and evaluation of mixing and combustion processes at total- and multi-dimensional levels. The results show that the best nozzle hole cone angle calculated by this method is 155°; the best nozzle hole number $\times$ hole diameter of injector is $8 \times 0.27\text{mm}$, and the best swirl ratio is 1.0; the calculation results and experimental results are consistent. Therefore, the combined combustion field-effect analysis method can be used to carry out quantitative evaluation on the performance of a combustion system and it has instructive significance to the optimal matching and improvement of a combustion system.

Key words: air-fuel mixing, combustion system, diesel engine, field-effect analysis, simulation

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1. Introduction

The in-cylinder physical fields, such as the velocity and the fuel concentration field, have significant impacts on the spray mixing process of diesel engines. If these fields can reach the optimal coupling effect through combustion system designing, the mixing process will be under control and thereby the combustion process can be improved (Heywood, 1988; Kang and Reitz, 1999; Micklow and Gong, 2007; Qiu et al, 2014; Rakopoulos et al., 2010; Pulkrabek, 2003).

The combustion process in a direct injection diesel engine is mainly diffusion combustion, which is determined by the diffusion and mixing rate of fuel. Actually, the air-fuel mixing process is a typical mass transfer process, while mass transfer and heat transfer are very similar in many respects. Referencing the field synergy principle proposed by

Professor Guo Zeng-yuan (Chen et al., 2008; Guo, 2000), Liu Fu-shui, Bai Bing and Li Xiang-rong, scholars at Beijing Institute of Technology, put forward a new mixing field-effect (or field synergy) analysis method which is used for quantitative research on the speed of mass transfer in the spray process of diesel engine. The results show that this method is feasible for evaluating spray and mixing process of the diesel engine (Liu et al., 2009).

Specifically, if the velocity direction of the flow field in the cylinder is identical with the gradient direction of fuel concentration, air-fuel diffusion and mixing will be speed up, and under this condition, the field effect is the strongest; otherwise, it is relatively weak. Guided by this theory, the quantitative analysis of mass transfer in the whole spray process of a combustion system was carried out and the result could be used as a reference for the optimization and matching of combustion systems

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(Li et al., 2011). However, the theory is only suitable for the conditions prior to the beginning of the combustion process because it assumes that the distribution of oxygen is even when analyzing the air-fuel mixing process.

Once the combustion process starts, the distribution of oxygen varies considerably from place to place in the cylinder, and the mixing effectiveness is only related to the air-fuel ratio. Thus one attempts to avoid excess fuel in places where oxygen is exhausted. Referencing experience with the spray mixing field-effect analysis method, this paper attempts to consider the influence of the oxygen concentration field and presents quantitative research on the role of mass transfer in the combustion process.

We expect to use the 'micro-perspective' and master the rule of changes of physical fields in the mixing process by means of simulation; explore approaches to organizing and utilizing the physical fields in the cylinder so as to accelerate diffusion combustion; and guide the design and optimal matching of a diesel engine combustion system to determine combustion chamber, air admission and fuel injection parameters.

2. Materials and methods

2.1. The principle of the field-effect analysis method for combined combustion

After the combustion begins, the speed of fuel diffusion from areas with higher oxygen-fuel ratio to areas with lower oxygen-fuel ratio decisively influences the subsequent combustion process. Thus, referencing experience with the spray mixing field-effect analysis method, the author has proposed the concept of the combined combustion field-effect angle: the intersection angle between the direction of oxygen-fuel ratio gradient and the direction of velocity vector is defined as the field-effect angle, which is used as a parameter to characterize the role of local field-effect (Fig. 1).

The dots (Fig. 1) indicate the nodes of a three-dimensional calculation grid; the curve is the contour line of oxygen-fuel ratio; the gradient direction of oxygen-fuel ratio is the normal direction of the contour line that passes the node, and in this paper, the reducing direction of the oxygen-fuel ratio is defined as positive.

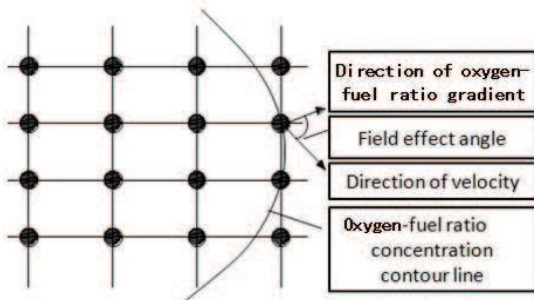


Fig. 1. The sketch map of field-effect angle

The smaller the field-effect angle is, the better the effect of mass transfer is, and the faster the diffusion mixing process will be.

The formula of field-effect angle for combined combustion is defined as Eq. (1).

$$\theta = \arccos \left(\frac{u \cdot \frac{d(f_c/O_c)}{dx} + v \cdot \frac{d(f_c/O_c)}{dy} + w \cdot \frac{d(f_c/O_c)}{dz}}{|\vec{U}| \cdot |\text{grad}(f_c/O_c)|} \right) \quad (1)$$

where: θ is the field-effect angle at a certain node;

u, v, w - velocity components of velocity $\vec{U}$ in three directions of x, y and z of coordinate; f_c - concentration of the fuel; O_c - concentration of the oxygen; $\text{grad}(f_c/O_c)$ - gradient of oxygen-fuel ratio, which is defined as the variation of oxygen-fuel ratio in unit distance. When the distribution of oxygen is even, the concentration gradient of oxygen in each direction is zero. The $\text{grad}(f_c/O_c)$ can be expressed as Eq. (2).

$$\text{grad}(f_c/O_c) = \frac{1}{O_c} \cdot \text{grad}(f_c) \quad (2)$$

At this point, the expression of the field-effect angle in the combined combustion field-effect analysis method is consistent with that of the field-effect angle of spray mixing field-effect analysis method described by (Liu et al., 2009).

2.2. Weighting treatment on the combined combustion field-effect angle

In CFD calculation, θ_i is the field-effect angle of No. i grid cell; n is the number of grid cells of the calculation model. Then, the mean field-effect angle θ_m can be described as Eq. (3).

$$\theta_m = \frac{\sum_{i=1}^n \theta_i}{n} \quad (3)$$

When f_c of local areas in cylinder is extremely low or high, θ_i will become very small or large. On the one hand, in areas where f_c is extremely low, there is only very limited amount of fuel to transfer, and if f_c is below the lean burn limit, mass transfer is meaningless. On the other hand, in places where f_c is extremely high, if U is too low, the fuel mass transfer process will become very slow and thus the fuel diffusion and mixing process will be less effective. Therefore, it is necessary to carry out weighting treatment to θ_i considering the inhomogeneity of the concentration field and velocity field. Also, because the grid

volume in calculation region is not totally homogenous, it is also necessary to conduct weighting treatment to θ_i .

The following describes the mass correction and time average of field-effect angle $\bar{\theta}_{mcvmj}$ with respect to weighted concentration, weighted velocity and weighted volume, as well as the integrated weighted average.

(1) θ_i with respect to weighted concentration

The fuel density in No. i grid cell is defined as $FDEN_i$, and in the calculation region, the maximum fuel density is $FDEN_{max}$ and the minimum fuel density is $FDEN_{min}$, and if the oxygen-fuel ratio is EQR_i and the minimum value of the oxygen-fuel ratio for ignition is Φ_1 , then the weighting coefficient of concentration k_i at No. i node can be described as Eq. (4).

$$\begin{cases} k_i = 1 & EQR_i \leq \Phi_1 \\ k_i = \frac{FDEN_{max} - FDEN_i}{FDEN_{max} - FDEN_{min}} & \Phi_1 < EQR_i \end{cases} \quad (4)$$

That is to say, k_i has a linear relation (1~0) to the fuel density between $FDEN_{max}$ and $FDEN_{min}$. If the fuel concentration is too low, the effect of mass transfer is regarded as 0, and namely k_i equals to 1.

(2) θ_i with respect to weighted velocity

Velocity is also carried out weighting treatment in the similar way above. The weighting coefficient k'_i ranges from 0 to 1. The better the effect of mass transfer is, the smaller k'_i will be. The velocity value of No. i grid cell is defined as V_i , the maximum and minimum fuel density are $FDEN_{max}$ and $FDEN_{min}$ respectively, then k'_i at No. i node should be defined as Eq. (5).

$$\begin{cases} k'_i = 1 & EQR_i \leq \Phi_1 \\ k'_i = \frac{V_{max} - V_i}{V_{max} - V_{min}} & \Phi_1 < EQR_i \end{cases} \quad (5)$$

That is to say, when $V_{min} \leq V_i \leq V_{max}$, k'_i linearly changes between 0 and 1.

(3) θ_i with respect to integrated weighted average concentration, velocity and volume

In the calculation region, the volume weighting coefficient of No. i grid cell is k''_i . Then, the field-effect angle of weighted concentration, weighted velocity and weighted volume of No. i grid cell is defined as Eq. (6).

$$\theta_{icvv} = k_i k'_i k''_i \theta_i \quad (6)$$

The field-effect angle with respect to integrated weighted average of concentration, velocity and volume is defined as Eq. (7).

$$\theta_{mcvv} = \frac{\sum_{i=1}^n k_i k'_i k''_i \theta_i}{\sum_{i=1}^n k_i k'_i k''_i} \quad (7)$$

(4) The mass correction of integrated weighted average field-effect angle θ_{mcvv}

Supposing that the quantity of residual fuel of No. j combustion system(at the same crank angle and running condition with different combustion chamber, nozzle cone angle, number of nozzles and diameter, swirl ratio) or of the crank angle(in the same combustion system at different crank angle) compared is m_j , and the maximum residual fuel of the several combustion systems or of crank angles compared is m_{max} , then the correction coefficient, i.e. k_{mj} , of No. j combustion system or the crank angle, should be defined as Eq. (8).

$$k_{mj} = \frac{m_j}{m_{max}} \quad (8)$$

The revised integrated weighted average field-effect angle θ_{mcvmj} is defined as Eq. (9).

$$\theta_{mcvmj} = k_{mj} \theta_{mcvv} \quad (9)$$

That is to say, the less the quantity of residual fuel is, the faster the diffusion combustion was.

(5) Time average

The integrated weighted average field-effect angle θ_{mcvmj} at each moment represents the impact of velocity field and concentration field on air-fuel mixing at the very moment; that is to say, the smaller the angle is, the more beneficial the synergy effect of physical fields on air-fuel mixing at that moment. Therefore, it is not enough to evaluate the performance of a combustion system with the integrated weighted average field-effect angle θ_{mcvmj} at only one moment; the entire combustion process requires a comprehensive assessment, i.e. the time average of the integrated weighted average field-effect angles $\bar{\theta}_{mcvmj}$ at all moments, defining as Eq. (10).

$$\bar{\theta}_{mcvmj} = \frac{\sum \theta_{mcvmj} \Delta \varphi}{\sum \Delta \varphi} \quad (10)$$

where: $\Delta\varphi$ - time step; $\bar{\theta}_{mcvmj}$ - time average of the integrated weighted average field-effect angle.

2.3. Simulation and experimental settings

In this paper, the study includes two stages: simulation stage and experimental stage. By applying to the field-effect analysis method, the former aims at studying the influencing mechanism of fuel injection parameters which influence the power, emission and economy performance of diesel engine significantly to the combustion process (Tiegang et al., 2008, 2009; Tiegang and Lee, 2011), and meanwhile finding out the optimal matching of these parameters for diesel engines which have 132mm diameter cylinders and use the double swirl combustion system. In the experimental stage, the experimental results are compared with the simulation results to verify the credibility and the practicability of the field-effect analysis method.

2.3.1. Simulation settings

The simulation research is carried out based on the double swirl combustion system (DSCS)(Li and Sun, 2010). The prototype of double swirl combustion chamber is demonstrated (Fig. 2) (Rong et al., 2000; Wei et al., 1998). This paper studies the rules influencing the effect of air-fuel mixing by changing one of the parameters of air intake and fuel injection factors, and using the integrated weighted average field-effect angle, the time average of integrated weighted average field-effect angle, and a certain parameter of the velocity field and fuel concentration field. All the computational grids are hexahedral; the grid scale of the combustion chamber within the piston roof is about 1mm (Fig. 3).

The boundary conditions for calculation are shown in Table 1. In the calculation, the turbulence model applies to k- ϵ model; the combustion model is EBU model; spray breakup model is WAVE model, $A = 5$, $C_2 = 10$. This study is based on AVL Company's 3D CFD software-Fire.

The 3D-Formula embedded tool is mainly used when carrying out field-effect analysis and calculation. The program for field-effect analysis and calculation should be input in line with the requirements of Fire software.

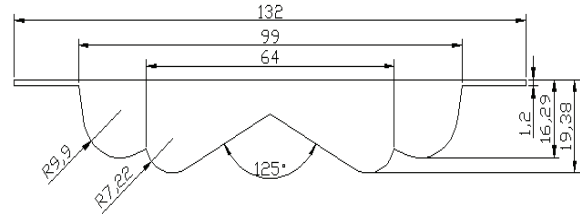


Fig. 2. The structure of DSCS chamber

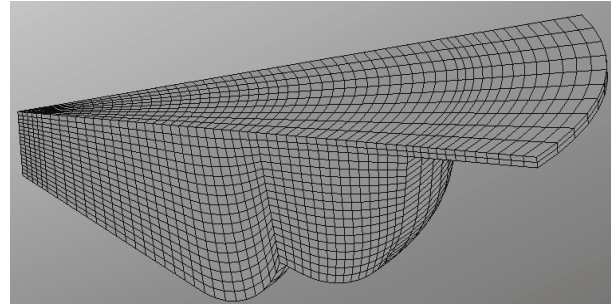


Fig. 3. The grid of DSCS chamber

Then, the cdfDerive, an assistant tool of Fire, is used to make post treatment upon the simulation results. By substituting the calculation results of cdfDerive into Eqs. (9) and (10) for calculating the field-effect angle, the field-effect angle can be worked out.

2.3.2. Experimental settings

The experiment has two purposes: one is to verify the correctness of the combined combustion field-effect analysis method; the other is to investigate to what extent the engine system will be improved by applying this method. The experiment is conducted on a single-cylinder 1132Z diesel engine. The basic parameters of the engine are shown in Table 2.

The engine uses an electronically controlled unit pump fuel injection system, and the maximum injection pressure is of 160MPa. The engine stand is an eddy current dynamometer with maximum power of 160kW, maximum torque of 650 N • m, and maximum speed of 6000r/min. A VHN-16/8 air compressor is used to simulate the air intake pressurized environment, while using AEH100 to heat the intake air.

Table 1. Main boundary conditions for calculation of field-effect

Engine speed	2500r/min	Initial angle for calculation	140° CA
Initial pressure in cylinder	0.42MPa	Initial temperature in cylinder	383K
Beginning of injection	352° CA	Injection duration	42° CA
Fuel delivery per cycle	281.6mg	Nozzle cone angle	155°(Except in section 3.1)

Table 2. The basic parameters of the diesel engine

Cylinder bore	132mm	Stroke	145mm
Length of connecting rod	262mm	Compression ratio	17
Fuel injector	8×0.27mm	Intake pressure	0.36 MPa
Intake temperature	333K		

3. Results and discussion

3.1. Results and analysis of field-effect with different nozzle cone angles

It can be seen that in the early stages of combustion, such as at the stage of 366 ° CA, the mass-revised integrated weighted average field-effect angles θ_{mcvmj} corresponding to each nozzle cone angle (140°, 145°, 150°, 155°, 160°, 165°, 170°) are basically the same; as mixing and combustion proceed, the matching conditions of different combustion systems begin to show their differences, the minimum value of θ_{mcvmj} occurs (Fig. 4). The best nozzle cone angle is between 155° and 160°, in which the air-fuel mixing effect is optimum (Fig. 4).

In addition, in order to facilitate the comparison between different nozzle cone angles in the graphic mode, the simulation result at 394° CA when the fuel spray finishes is chosen for analysis (Fig. 6).

In the bottom clearance area, if the nozzle cone angle is too small, there will be too little fuel distributed here, resulting in low utilization rate of the air in the region, so that the effect of air-fuel mixing is harmful and the role of field-effect is not obvious. If the nozzle cone angle is too big, too much fuel will enter into the bottom clearance area, where the strength of the reverse squish flow is relatively low and the diffusion of fuel is not obvious, worsening the combustion performance of the reverse squish flow zone.

In the area near the combustion chamber center and the arc ridge, when the nozzle cone angle increases, the high field-effect zone moves outward along the radial direction. Similarly, if the nozzle cone angle is too small, there will be not enough low-fuel area for mass transfer moved inward.

In the area near the bottom of the cylinder head, if the nozzle cone angle is too small, the area is of low velocity, low fuel concentration and low field-effect, which is very detrimental to rapid air-fuel mixing. With the increase in nozzle cone angle, the situation will be significantly improved; however, if the nozzle cone angle is too large, the fuel tends to attach to the underside of the cylinder head, which is not conducive to diffusion. Considering all these

factors, for the matching of this combustion chamber, there must be an in-between nozzle cone angle which can give full play to the role of integrated field-effect. That is to say, the synergy effect of all physical fields on air-fuel mixing and combustion is the best in the reverse squish flow area, near the cylinder center and the bottom of the cylinder head, and in the double swirl arc ridge area.

3.2. Results and analysis of field-effect with different number of nozzles and diameter

According to the different number of nozzles, different models are established: a 12-nozzle-hole fuel injector corresponds to the establishment of 1/12 model; similarly, n-nozzle-hole fuel injector corresponds to 1/n model. Under the condition that the total mass of fuel injected is unchanged and the total flow area is basically the same, six groups with different number of spray nozzle holes $\times$ nozzle hole diameter are chosen, i.e. 4 $\times$ 0.38mm, 5 $\times$ 0.34mm, 6 $\times$ 0.31mm, 8 $\times$ 0.27mm, 10 $\times$ 0.24mm, and 12 $\times$ 0.22mm, respectively. The nozzle cone angle is 155°CA (Table 1). The parameter of the fuel injector 8 $\times$ 0.27mm is the best for engine performance because the field-effect angle is the smallest (Figs. 7 and 8).

The 394° CA, i.e. the integrated weighted field-effect angle θ_{icvv} when the fuel spray just finishes, is taken for comparison (Fig. 9). The results show that if there is only a very small number of nozzle holes, too much fuel will stay in the bottom clearance region, where the gradient of fuel concentration is very small. This is not conducive to further air-fuel mixing. With the increase in nozzle holes, the swirl in the vicinity of the arc ridge is enhanced and areas with higher field-effect become larger, which is conducive to the use of the air in the inner part of the double swirl combustion chamber, indicating that the air-fuel mixing process is sped up here. However, if there are too many nozzle holes, although a relatively higher field-effect zone can be produced in the vicinity of the central region of the cylinder and near the bottom of cylinder head, yet the field-effect in the reverse squish flow area and the bottom clearance area is relatively weak. This again is not conducive to air-fuel mixing.

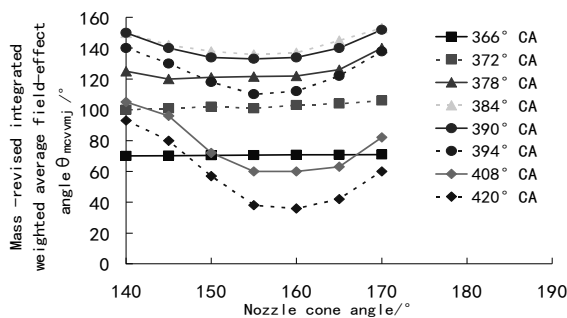


Fig. 4. Comparison of θ_{mcvmj} with different nozzle cone angles

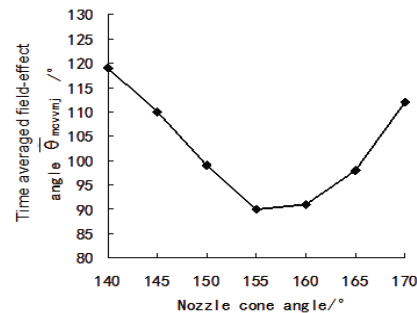


Fig. 5. Comparison of θ_{icvv} with different nozzle cone angles

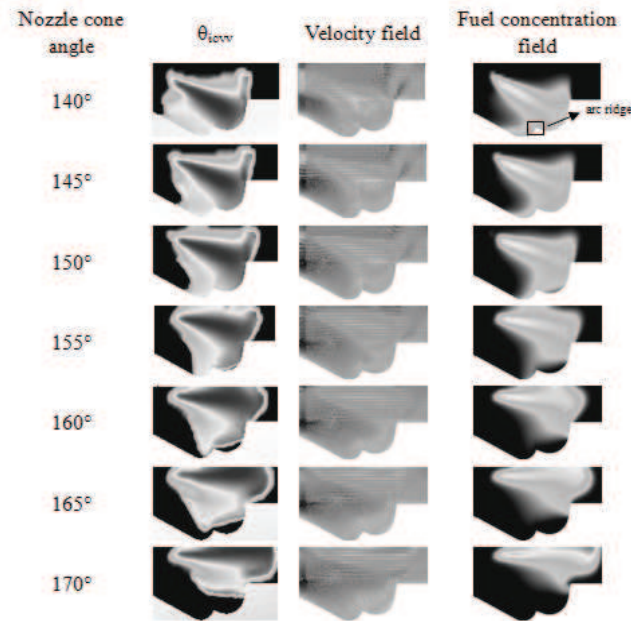


Fig. 6. Simulation results at 394°CA with different nozzle cone angles

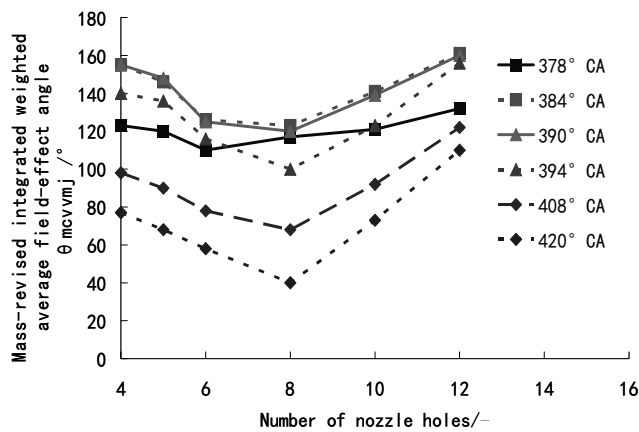


Fig. 7. Comparison of θ_{mcvnmj} with different numbers of nozzle holes

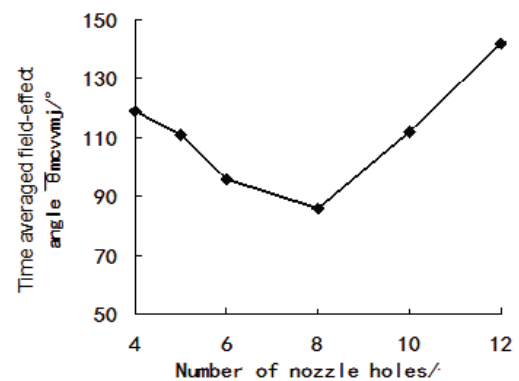


Fig. 8. Comparison of with different numbers of nozzle holes

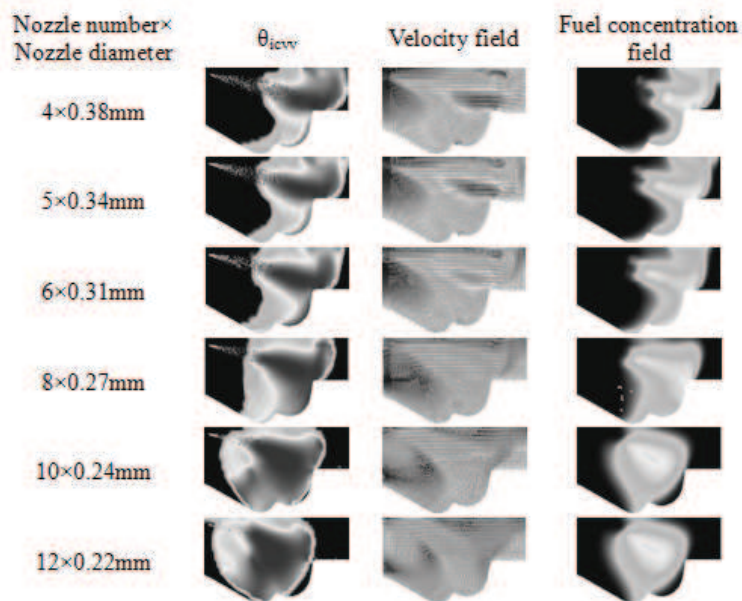


Fig. 9. Simulation results at 394°CA with different numbers of nozzle holes

In summary, there is an optimal number of spray holes making the best of the integrated field-effect. In this study, the best combination of nozzle hole numbers and nozzle hole diameter is $8 \times 0.27\text{mm}$.

3.3. Calculation results and analysis of field-effect with different swirl ratios

In the early combustion stage (Fig. 10), such as at 378° CA, the greater the swirl ratio (swirl and engine speed ratio at the moment when intake valve is fully closed), the more conducive it is to air-fuel mixing, because the increase in swirl ratio helps to speed up air-fuel mixing.

With the advance of the combustion process, too large a swirl ratio will weaken the role of field-effect because a larger swirl ratio can lower the penetration capacity of fuel spray, thus decreasing the diffusion of fuel in the radial direction. The best swirl ratio is of 1.0, and then the time averaged field-effect angle $\bar{\theta}_{mcvmj}$ is the smallest (Fig. 11).

The 394° CA crank angle, i.e. the integrated weighted field-effect angle θ_{icvv} when the fuel spray just finishes, is taken for comparison. In the axial direction of the combustion chamber (Fig. 12a): with the increase in swirl ratio, the area of high field-effect zone reduces and the synergy effect of all physical fields weakens; in places where the fuel concentration is relatively high, if the swirl ratio is also high, the velocity of flow field will be small, which is not conducive to the air-fuel mixing in the axial and radial directions.

In the circumferential direction of combustion chamber (Fig. 12b): if the swirl ratio is too small, fuel diffusion and mixing will not be obvious; as the swirl ratio increases, the area of high field-effect zone increases too, which is conducive to air-fuel mixing in the circumferential direction; however, if the swirl ratio is too large, the fuel distribution areas of adjacent fuel spray will overlap and gradually interfere with each other, resulting in too thick local

fuel and air mixture, which is not conducive to air-fuel diffusion and the mixing process. This establishes an optimal swirl ratio for the best engine performance. We found the best swirl ratio of 1.0.

3.4. Validation of the Simulation Model

Experiment is carried out for validating of the simulation model, conditions is shown in Table 3. From the experimental results of in-cylinder pressure and the instantaneous heat release rate with different nozzle cone angles (Figs. 13 and 14), it can be seen from the figures that when the nozzle cone angle is 155° , within the range of 20° CA after TDC, the cylinder pressure has been higher than that at other nozzle cone angles. Meanwhile the instantaneous heat release rate is the highest, indicating that at a 155° nozzle cone angle, fuel burns and releases heat the fastest.

When the nozzle cone angle is 155° , the fuel spray is divided into two part by the arc ridge, one small part goes into the inner area of the combustion chamber in the clockwise direction and mixes with the air, the other part of the spray goes into the outer area of the combustion chamber in the anti-clockwise direction and mixes with the air (Fig. 6). Under this condition, the fuel mixes with the air more homogeneously and air utilization ratios inside and outside the cylinder match optimally, so that the air-fuel mixing speed is the highest. The analysis of the instantaneous heat release rate can also explain the differences of cylinder pressure curves.

Fig. 15 shows that the fuel consumption and field-effect angle at 155° nozzle cone angle are lowest, indicating that the engine performance is at its best at this condition.

Fuel consumption is derived from Eq. (11).

$$b_e = B / P_e \quad (11)$$

where: b_e - fuel consumption(g/kW.h); B - fuel supply quantity (kg/h); P_e - effective power(kW).

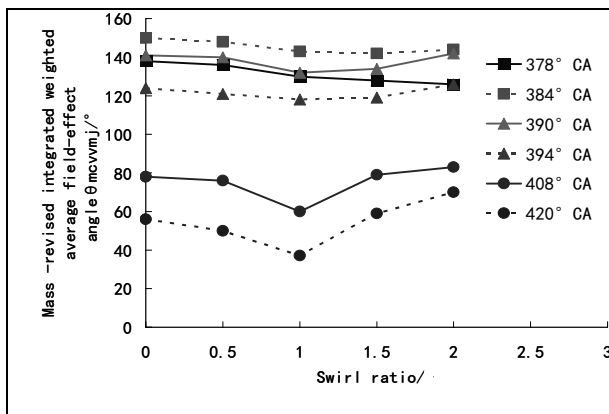


Fig. 10. Comparison of θ_{mcvmj} with different swirl ratios

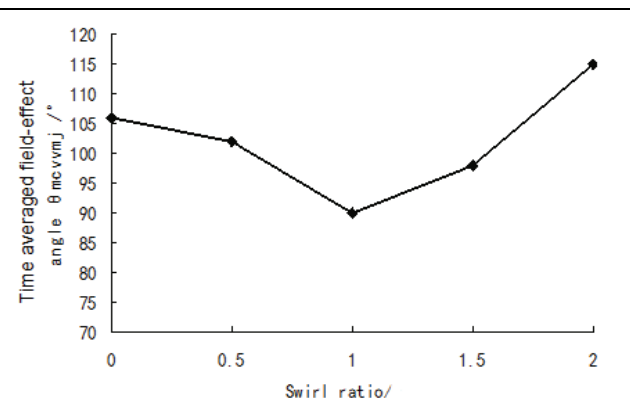


Fig. 11. Comparison of $\bar{\theta}_{mcvmj}$ with different swirl ratios

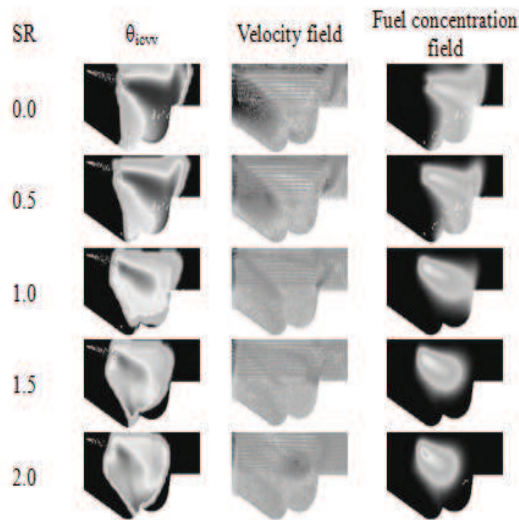


Fig. 12a. Simulation results at 394°CA with different swirl ratios

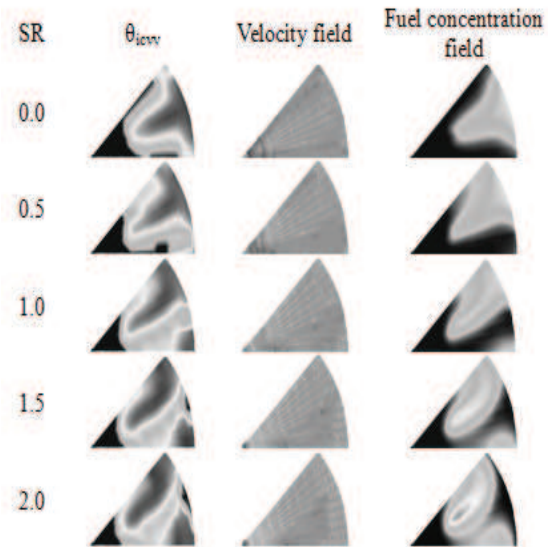


Fig. 12b. Simulation results at 394°CA in circumferential direction with different swirl ratios

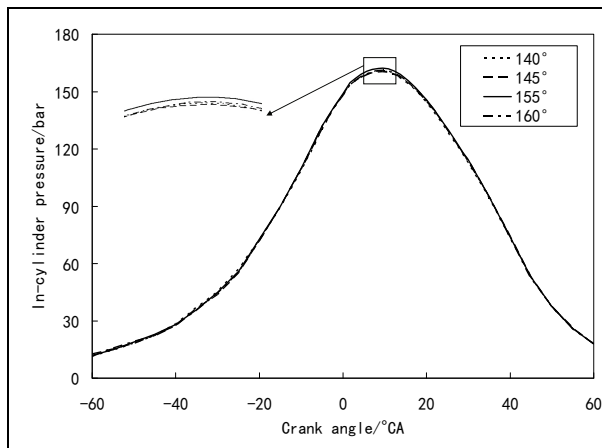


Fig. 13. Comparison of pressure in cylinder with different nozzle cone angles

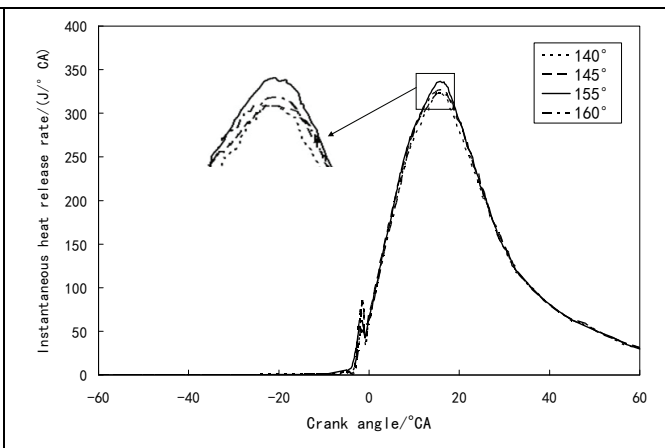


Fig. 14. Comparison of instantaneous heat release rate with different nozzle cone angles

Table 3. Operating conditions

<i>Engine speed</i>	2500r/min	<i>Initial pressure</i>	0.36MPa
<i>Beginning of injection</i>	352° CA	<i>Initial temperature</i>	383K
<i>Fuel delivery per cycle</i>	281.6mg	<i>Injection duration</i>	33° CA

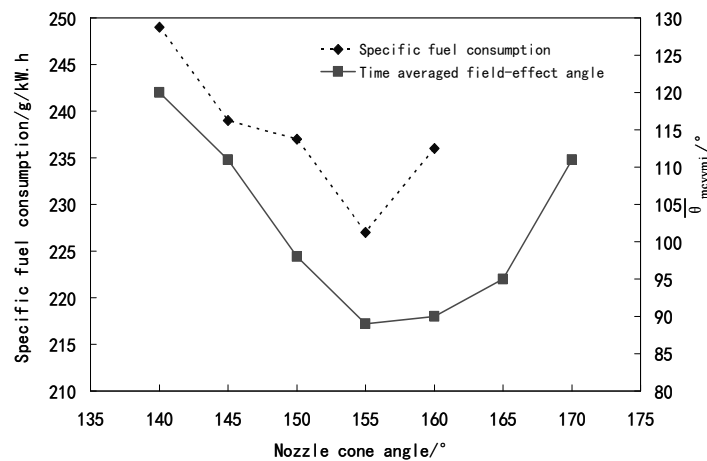


Fig. 15. Comparison of $\bar{\theta}_{mcvnmj}$ and of specific fuel consumption with different nozzle cone angles

4. Conclusions

Based on the former spray mixing field-effect analysis method, this paper has proposed a new method for the evaluation of the diesel engine combustion process, i.e. a combined combustion field-effect analysis method.

The method can be used to carry out quantitative analysis and evaluation on the performance of a combustion system and then find out a way how to take advantage of field synergy effect to promote air/fuel transfer process by changing combustion chamber, air admission and fuel injection parameters.

Calculation results have important reference value for the further improvement of combustion systems.

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FORECASTING THE PRESENCE OF Ca^{2+} AND Mg^{2+} CATIONS IN MINERAL WATERS. A MODEL BASED ON FUZZY LOGIC

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Abstract

This paper aims to develop the theoretical framework and the applicative implementation of a new analysis method, which has the purpose of determining and classifying mineral waters in Romania and Europe, with the use of mathematical modelling and fuzzy logic. Firstly, the article underlines the properties of mineral waters in terms of curative effects, particularly the role of Ca^{2+} and Mg^{2+} upon the human metabolism. The values of these two chemical elements will constitute an index, a basis for creating a comparative database, which will embed a limited number of samples, with statistical value; in brief, a mathematical model that determines the mineral water spring (or springs) has been implemented, which in the same time illustrates graphically the membership degree of an unknown water sample to a specific spring, making use only of the Ca^{2+} and Mg^{2+} concentration indexes.

Key words: Ca^{2+} concentration, fuzzy logic, genetic algorithms, ionic stability, Mg^{2+} concentration, mineral water

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1. Introduction

In terms of biophysics and biochemistry, the normal functions of the human body require that a number of nineteen minerals have to be found in proper concentrations and in precise homeostasis. These elements are: molybdenum, chlorine, fluorine, phosphorus, selenium, iodine, manganese, copper, magnesium, potassium, zinc, iron, calcium, sodium, vanadium, silicon, boron, nickel and chromium (World Health Organization, 2011). When the inbond/outbond flow of these elements is unbalanced, various physiological malfunctions occur, some of them with prolonged and serious consequences for the human health (Sipos et al., 2012). A major source for some of the above essential constituents is the drinking water, whose concentration in minerals may vary significantly from a certain spring or region to another. These

sources of mineral water represent the core of a prosperous economic activity in several countries (among which Romania is included), which basically exploits the springs, bottles the water in various forms of packaging and, through different food chains, supply the bottled mineral water for consumption to the population.

According to literature (World Health Organization, 2005), during the transit through all the nodes of the food chain (bottling factory, en-gross supplier, retail store etc.), a matter of permanent concern is represented by the purity of the bottled mineral water, which has to strictly adhere to the composition of the genuine spring or geographical source, priorly determined and published by renown international laboratories. These procedures are traditionally laboratory-based measurements for chemical components, which are time-consuming and require expensive equipment and consumables.

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Finding new approaches and improving the existent ones for the fast and exact determination of the composition of mineral waters is a matter of interest (Sipos et al., 2012).

Among modern trends in the area of water or land quality assessment are the ones based on fuzzy logic (Gharibi et al., 2012; Melendez-Pastor, 2013). Fuzzy logic is a domain which deals with a rather approximate perspective upon the process of reasoning and attribution of labels, and, according to Zadeh, it represents an “extension of multivalued logic”. The purpose of the fuzzy logic is to formalize the way in which reasoning is performed, starting from the principle that the modes of reasoning are approximate rather than exact numbers: “everything, including truth, is a matter of degree” (Zadeh, 1988).

Basically, fuzzy logic-based water quality evaluation identifies parameters with relevance on human physiology and, though specific programming, generates a database (an index) with visible “fingerprints” for each of these parameters. An analysed sample of mineral water with identified “fingerprints” would later be cross-compared with this index, thus generating a composition report which can be used for identifying the source of the sample by comparing it with the official source composition. This research, from a variety of physicochemical, microbial, and toxicological parameters which could be considered as possible candidates for fuzzy logic programming, has selected Ca^{2+} and Mg^{2+} for their recognized critical importance and their potential impact on human health. The behaviour of these parameters has been

used to program a fuzzy-logic assessment method for analysing the quality of the composition of mineral waters, which has yielded accurate and reliable laboratory results.

2. Literature review

The definition of natural mineral water (as specified in the European directive 80/777/EEC) is the microbiologically wholesome water that streams from an aquifer located underground and which is tapped using one or several wells, which may be either natural or manmade. The treatment of natural mineral water prior to the bottling process is limited to the removal of unstable components (e.g. sulphide, iron) and to the reintroduction of carbon dioxide in its composition. Furthermore, a distinction is made between “spring water” (which contains only a few minerals and comes from a natural source) and “mineral water” (which is bottled at the source and has to have at least 150 mg of minerals per litre). These standards, however, vary from one country to another (World Health Organization, 2005).

2.1. The importance of magnesium for the human organism (Mg^{2+})

The daily dietary ratio of magnesium for an adult is about 3-400 milligrams. Almost all cells inside the human body contain a certain amount of magnesium (Combs, 2006). Magnesium is involved in the transmission of nervous impulses and regulates the muscle contractibility.

Table 1. Comparative analytical data on the chemical characterisation of mineral water sources in Europe and the eastern Mediterranean region (Ştefanache, 2002)

No.	Origin and source	Mineralisation mg/L (sum of ions)	Chemical characterisation (Chemical dominance)	$\text{Ca}^{2+}/\text{Mg}^{2+}$ mg/L	$\text{Ca}^{2+}/\text{Mg}^{2+}$ mEq %
Italy					
1	Pejo – Fonte Alpina	90.35	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	3.2	1.945
2	Crodo Lisiel	255.7	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	8.47	5.15
3	Flaminia Nocera Umbra	313.97	HCO_3^- , Ca^{2+} , Mg^{2+}	30.82	18.73
4	Fabia Terni	575.5	HCO_3^- , Cl^- , Ca^{2+} , Na^+ , Mg^{2+}	26.32	16.02
France					
5	Vittel	957.75	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	5.61	3.41
6	Pierval	447.7	HCO_3^- , Cl^- , Ca^{2+} , Mg^{2+}	24.04	13.83
Belgium					
7	Spa	28.48	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	2.56	1.55
Germany					
8	Original	418.72	HCO_3^- , Ca^{2+} , Mg^{2+}	1.73	1.05
Spain					
9	Font Vella – Girona	239.5	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	5.24	3.14
10	Bezoya (Madrid)	28.8	HCO_3^- , Cl^- , Na^+ , Ca^{2+} , Mg^{2+}	9.0	5.4
11	Fontdor (Girona)	50.4	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	6.15	3.75
Hungary					
12	Apenta	2340.5	HCO_3^- , SO_4^{2-} , Na^+ , Ca^{2+} , Mg^{2+}	5.91	3.82
13	Kristalyviz	1667.5	HCO_3^- , Cl^- , Ca^{2+} , Na^+ , Mg^{2+}	8.64	5.25
Yugoslavia					
14	Mineral Radenska	2389.1	HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+}	2.28	1.38

Table 2. Comparative analytical data on the chemical characterisation of mineral water sources in Europe and the eastern Mediterranean region (Ştefanache, 2002)

No.	Origin and source	Mineralisation mg/L (sum of ions)	Chemical characterisation (Chemical dominance)	$\text{Ca}^{2+}/\text{Mg}^{2+}$ mg/L	$\text{Ca}^{2+}/\text{Mg}^{2+}$ mEq %
Greece					
15	<i>Epitropezio – Nero</i>	398.65	HCO_3^- , Ca^{2+} , Mg^{2+}	3.13	1.90
16	Loutraki – ivi	608.78	HCO_3^- , Cl^- , Ca^{2+} , Mg^{2+}	0.044	0.026
17	Sariza	348.2	HCO_3^- , Cl^- , Ca^{2+} , Na^+ , Mg^{2+}	3.18	1.93
Jordan					
18	<i>Kwter</i>	365.4	Cl^- , HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+}	0.98	0.59
19	Safa	592.78	Cl^- , HCO_3^- , SO_4^{2-} , Na^+ , Ca^{2+} , Mg^{2+}	1.59	0.96
Palestine					
20	<i>Eden</i>	340.8	HCO_3^- , Cl^- , Ca^{2+} , Na^+ , Mg^{2+}	3.33	2.02
21	Neviot	376.67	HCO_3^- , Cl^- , Ca^{2+} , Mg^{2+}	3.62	2.26
Turkey					
22	Hayt (Life)	165.8	HCO_3^- , Ca^{2+} , Mg^{2+}	5.5	3.34
Syria					
23	<i>Dreikiche</i>	216.54	HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+}	15.1	7.52
Romania					
24	<i>Borsec</i>	2334.6	HCO_3^- , Ca^{2+} , Mg^{2+}	3.2	1.98
25	Poiana Negri	1792.92	HCO_3^- , Ca^{2+} , Na^+ , Mg^{2+}	5.33	3.23
26	Calatis	654.75	HCO_3^- , Cl^- , Mg^{2+} , Ca^{2+}	1.3	0.75
27	Ana Vie	1717.0	HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+}	4.15	1.19
28	Izvorul Alb	195.7	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	10.65	6.54
29	Izvorul Minunilor still water	264.85	HCO_3^- , Cl^- , Ca^{2+} , Mg^{2+}	8.49	5.16
30	Izvorul Minunilor carbonated water	267.32	HCO_3^- , Ca^{2+} , Mg^{2+}	5.17	3.14
31	Amfiteatru	882.3	HCO_3^- , SO_4^{2-} , Mg^{2+} , Ca^{2+}	0.37	0.22
32	Pârcovaci spr. 1	798.48	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	3.24	1.96
33	Pârcovaci spr. 2	863.18	HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+}	2.29	1.39

It also activates the energy-producing enzymes (ATP generation). It is an element that protects the blood vessels, lowering the risk of a heart attack, and it also fortifies the bone structure. Magnesium deficiency is a serious situation, people who suffer from this usually experience lack of concentration, headaches, nervousness, dizziness and migraines (World Health Organization, 2005). The drinking water's concentration of magnesium varies between 20 and 1000 mg/L (Olivares and Uauy, 2004).

2.2. The importance of calcium for the human organism - Ca^{2+}

The daily dietary ratio of calcium for an adult is of about 800 milligrams. Special attention must be given to adolescents between 15-20 years old, because they require a greater amount of calcium per day (Combs, 2006). The calcium's importance for the human body derives from its implications in stabilizing cell membranes, teeth and bones, prevention of blood clots, transmission of muscle and nerve impulses. If the daily ratio isn't covered, in time, pathologies such as osteoporosis and spontaneous fractures might occur (Ong, 2004). Drinking water usually contains between 25 and 100 mg/L of calcium (Wurts, 1993). In some regions, where extra calcium is added, the total concentration is up to 500 mg/L (Olivares and Uauy, 2004).

To conclude, in order to protect people's health, special attention should be paid to the level of

minerals in the drinking water. They have an essential role in maintaining the body's homeostasis.

Moreover, a series of measures aiming to keep optimal levels of minerals in the potable water must be implemented. The stabilisation of corrosive, demineralised water should be realised by means of chemical substances that have the role to maintain or re-establish the magnesium and calcium optimal levels (Azoulay et al., 2004). The composition of bottled water and public supplies should be supervised and checked regularly by public health specialists who observe any concentration irregularities. Public health investigators should often conduct population studies in order to evaluate the impact the drinking water has on people. Through epidemiological studies, they should periodically analyze the magnesium, calcium and trace elements levels (World Health Organization, 2011). Although many studies on the mineral level of the water we drink have been conducted in different geographical areas in order to identify and understand the connection with several pathologies, unfortunately, the relationship between the deficiency or overexposure to various mineral elements and their health implications isn't completely clear nowadays (Radosavlevici, 2013).

3. Materials and methods

As a mathematical framework, the implementation of a classical fuzzy system has been chosen, which will have the purpose of determining

the source of an unknown water sample, using only information about the Ca^{2+} and Mg^{2+} concentration; the main advantage of this method is the fact that it reduces the costs implied by a classical determination of a mineral water source.

Fuzzy logic is a sub-domain of computational intelligence, which often refers to “a particular control engineering methodology, that exploits a numerical representation of commonsense control rules, in order to synthesize, via interpolation, a control law” (Ralescu and Shanahan, 1999).

As a programming environment, the Fuzzy Toolbox of Matlab (version r2011a) program has been chosen; Microsoft Office Excel program was also employed, in order to create sorted databases of the springs, ranked by the Ca^{2+} value and the Mg^{2+} , respectively.

4. Experimental

At a first stage, a database has been implemented, containing data from 31 springs, located in Romania, Europe and the eastern Mediterranean region, each one of them having a particular curative effect, therefore a significant value of the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio. These data have been collected from scientific literature (Ștefanache, 2002), the Ca^{2+} and Mg^{2+} concentration values (mg/L) being the values of interest. In order to obtain suitable inputs for the fuzzy system, two databases have been created, in which the springs were ranked in an ascending order, according to the cations' value.

The fuzzy system is a Mamdani type, model which imposes that the input variables are defined as

intervals, and not as single values. This model is mandatory for this projects' subject, due to the fact that a natural process relates to continuous variables – the indexes of chemical components from a mineral water may vary, as several external factors influence their concentration.

The implemented system has two inputs, “calcium” and “magnesium”, each one of them having 31 membership functions, labelled as follows: “COUNTRY ACRONYM_NAME OF THE SPRING_CATION”. Fig. 1 represents the block scheme of the FS (Fuzzy System), as well as the settings that have been applied.

The “max” type aggregation has been employed: the aggregation represents the set of operations by which the fuzzy sets are combined, in order to generate a single fuzzy set (output). The implication operators are, in classical logic, defined as the “If-Then rules” (Takagi and Sugeno, 1985). The most frequently chosen defuzzification method is the centroid one, in which the result is obtained by computing the centroid of each of the viable candidates.

The following steps consisted in defining the input variables: the first variable is named “calcium” and represents the Ca^{2+} concentration (mg/L); the second input, “magnesium”, is the expression of the Mg^{2+} concentration of the unknown mineral water sample (mg/L).

There can be used alternative combinations as inputs for the system, depending on the most convenient way to obtain the data: for the second variable, for example, alternatively, the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio may serve as an input for the system.

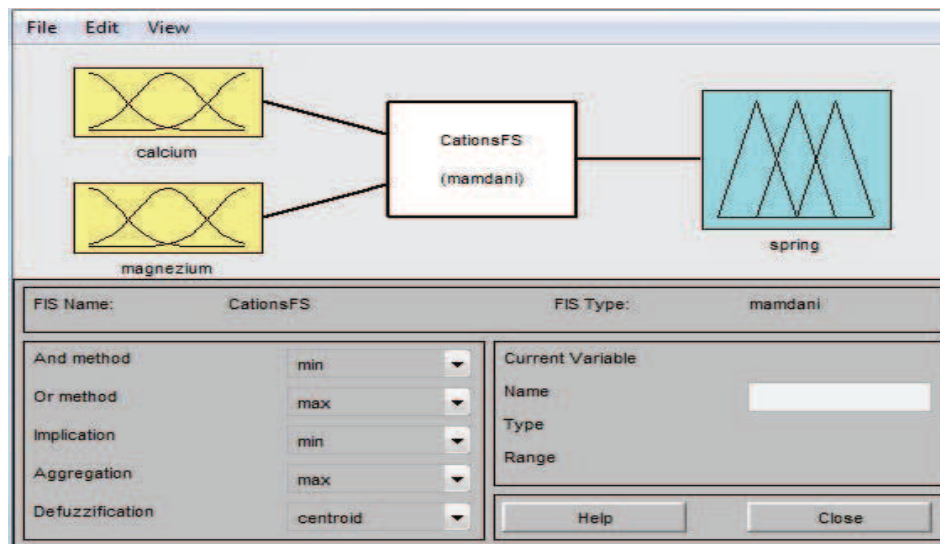


Fig. 1. Graphical overview of the fuzzy system, implemented in the Matlab Fuzzy Toolbox; input and output membership variables are illustrated, as well as the system's settings



Fig. 2. A general model of a fuzzy system, applied for two inputs

The functions associated to each membership function are “trimf”- type (triangular); the peak value is exactly the value retrieved from the database. The output value is $Y = \text{“spring”}$.

The number of linguistic degrees is 31, both for “calcium” as well as for “magnesium”, and are further defined and represented in subsections 3.1 and 3.2.

3.1. Membership functions for the input variable “calcium”

The input variable “calcium” of the fuzzy system has a number of 31 membership functions, corresponding to the total number of springs existent in the database. All the values have a triangular shape, the peak value corresponds to the calcium index experimentally measured from a sample; the limits of the intervals correspond to the maximum and minimum value of calcium index that could be attributed to a certain spring. In what follows, the “calcium” vector is detailed, by specifying each name of the membership variables (as they have been named in the fuzzy system), followed by the interval of confidence: between the square brackets, the numbers represent the minimum value of calcium

index, peak value (or the value experimentally determined), and the minimum value associated with each spring.

3.2. Membership functions for the input variable “magnesium”

Similarly with the vector “calcium” detailed above, the input variable “magnesium” of the fuzzy system has a number of 31 membership functions, corresponding to the total number of springs existent in the database that has been created. The graphical representation of each membership function is triangular, the peak value corresponds to the magnesium index experimentally measured from a sample; the limits of the intervals correspond to the maximum and minimum value of magnesium index that could be attributed to a certain spring. Below, the “magnesium” vector is explained, by specifying each name of the membership variables (as they have been named in the fuzzy system), followed by the interval of confidence: between the square brackets, the numbers represent the minimum value of magnesium index, peak value (or the value experimentally determined), and the minimum value associated with each spring.

Table 3. Indicatives and intervals of reference corresponding to each spring in the database, for the variable “calcium”

<i>Spring indicative</i>	<i>Min reference</i>	<i>Peak reference</i>	<i>Max reference</i>
SP BEZOYA ca	2.4	2.7	3.1
BE SPA ca	3.0	3.33	4
GR LOUTRAKIIVI ca	3.5	4	12
IT PEJO FA ca	10	13.23	20
HKJ KWTER ca	16	22.4	28
SP FONTDOR ca	20	24	30
TR HAYAT ca	21	29.7	35.2
SYR DEIKICHE ca	28	34	40
RO AMFITEATRU ca	30	35.2	42
SP FVGIRONA ca	34	40.9	46
PS EDEN ca	36	43.7	50
RO IZVMINCARB ca	40	45	52
DE ORIGINAL ca	40	45.2	53
GR SARIZA ca	40	46.2	56
RO IZVORULALB ca	42	49.5	56
IT CRODO LISIEL ca	45	50	57
RO IZVMINPLATA ca	45	50.12	58
HKJ SAFA ca	46	51.3	59
PS NEVIOT ca	50	58	65
RO CALATIS ca	53	60.12	67
GR EPITROPEZIO N ca	55	62.52	69
IT FLAMINIA N ca	62	69.35	76
FR PIERVAL ca	65	101	120
YUG MINERAL RAD ca	90	108.7	130
RO ANA VIE ca	92	112	135
IT FABIA TERNI ca	100	129	145
HU KRYSTALYVIZ ca	140	179	195
FR VITTEL ca	185	202	230
RO POIANA NEGRI ca	200	221.5	250
HU APENTA ca	210	230	300
RO BORSEC ca	300	347.7	370

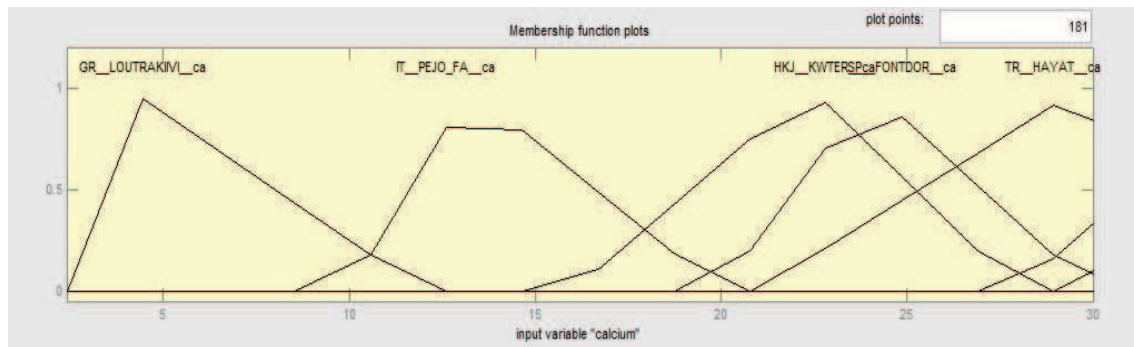


Fig. 3. Graphical representation in the Matlab Fuzzy Toolbox of the membership functions for the input variable “calcium” (zoomed figure, displaying 1/6 of the input variable “calcium”)

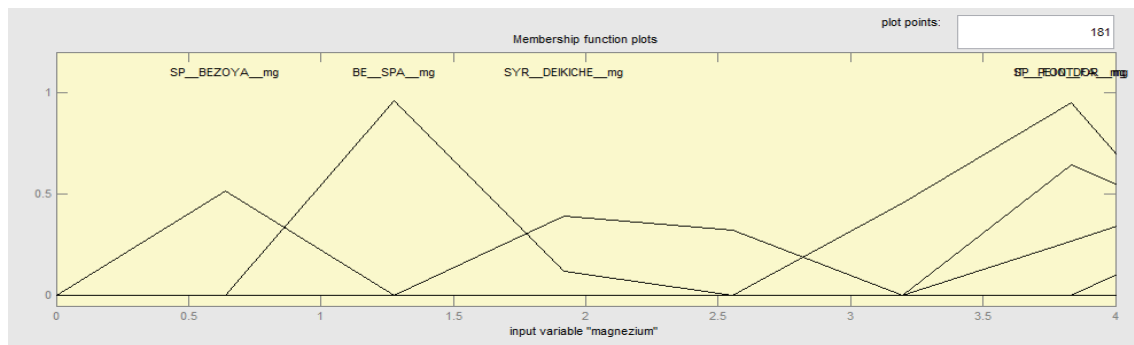


Fig. 4. Graphical representation in the Matlab Fuzzy Toolbox of the membership functions for the input variable “magnesium” (zoomed figure, displaying 1/6 of the input variable “magnesium”)

Table 4. Indicatives and intervals of reference corresponding to each spring in the database, for the variable “magnesium”

<i>Spring indicative</i>	<i>Minimum reference</i>	<i>Peak reference</i>	<i>Maximum reference</i>
SP_BEZOYA mg	0	0.3	1
BE_SPA mg	0.75	1.3	2
SYR_DEIKICHE mg	1.7	2.25	2.7
SP_FONTDOR mg	2.6	3.9	4.4
IT_PEJO_FA mg:	3.3	4.13	4.6
FR_PIERVAL mg	3.7	4.2	4.8
IT_FABIA_TERNI mg	4.2	4.9	5.6
TR_HAYAT mg	4.8	5.4	6
IT_CRODO_LISIEL mg	5.4	5.9	6.5
RO_IZVMINPLATA mg	5.4	5.9	6.5
RO_IZVORULALB mg:	5.7	6.1	6.8
SP_FVGIRONA mg	6.8	7.8	8.5
IT_FLAMINIA_N mg	7.3	8.25	8.9
RO_IZVMINCARB mg	8	8.7	11
PS_EDEN mg	10.5	13.1	14.8
GR_SARIZA mg	12.8	14.6	15.5
PS_NEVIOT mg	14.8	16	18
GR_EPITROPEZIO_N mg	17.8	19.95	21.5
HU_KRYSTALYVIZ mg	19	20.7	22.5
HKJ_KWTER mg	20.8	22.8	25
DE_ORIGINAL mg	24	26.1	31
HKJ_SAFa mg	29	32.5	35
FR_VITTEL mg	34	36	40
HU_APENTA mg	35	38.9	43
RO_POIANA_NEGRI mg	38.5	41.5	44
RO_CALATIS mg	42.5	46.2	49
YUG_MINERAL_RAD mg	44	47.6	54
RO_ANA_VIE mg	49	57	80
GR_LOUTRAKIIVI mg	65	89.98	96
RO_AMFITEATRU mg	90	94.3	110
RO_BORSEC mg	95	108.6	115

For the output (variable “spring”), equally-large intervals have been defined, the output membership functions being labelled similarly with the input membership functions: COUNTRY INDICATIVE_NAME OF THE SPRING. Fig. 5 illustrates a close-up of the output variable.

The next step consisted in implementing the inference, the rules set is defined with the “and” operator, thus obtaining a number of 31 rules, the combinations that will not be included in this set of rules will receive the default “null” value.

The fuzzy implementation approach for mineral waters can be further used as a base for a closed loop controller, in the process of drinkable water treatment, in order to maintain the level of elements at desired parameters (Gharibi et al., 2012; Fu, Huang, Zhu and Li, 2014). Fuzzy systems are successfully implemented in combination with artificial neural networks, being used in prediction applications (neuro-fuzzy predictors) (Neagu et al., 2002; Yan et al., 2012).

Other improved approaches of the fuzzy model have been implemented, such as the inclusion of uncertainties in the system, treated as multiple fuzzy boundaries (Huang and Jin, 2014).

4. Results and discussion

The graphical representation (surface-type) of the fuzzy system does not contain vertical lines, which indicated the fact that the system is a valid one (see Fig. 7). Furthermore, it can be observed that the representation does not have vertical lines or vertical asymptotes, which shows that for each input we have a determined output, whether it is a value embedded in the database or a null response.

By observing the overall tendency of the surface, it can be noticed, as in the figures with the membership function plots (Fig. 3 and Fig. 4), that most of the springs have a calcium concentration between 50 and 150, and a high magnesium index (over 100).

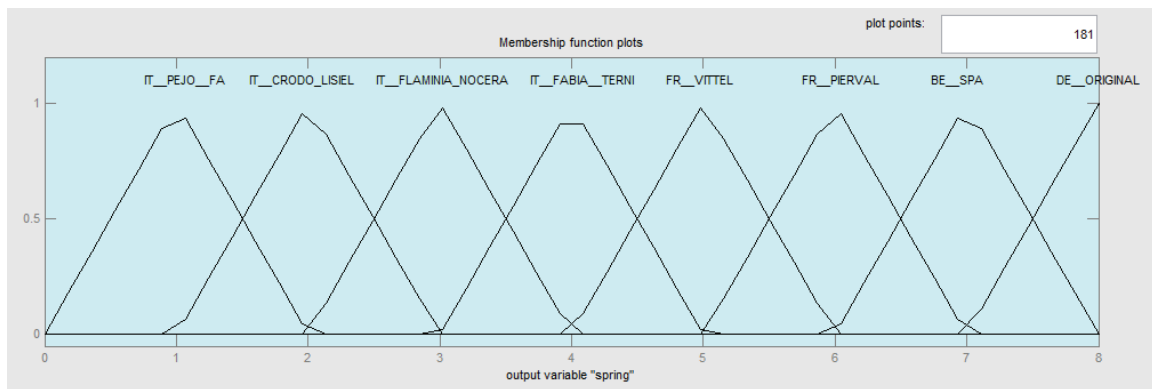


Fig. 5. Graphical representation in the Matlab Fuzzy Toolbox of the membership functions for the output variable “spring” (zoomed view, illustrating 1/4 of the total output membership functions)

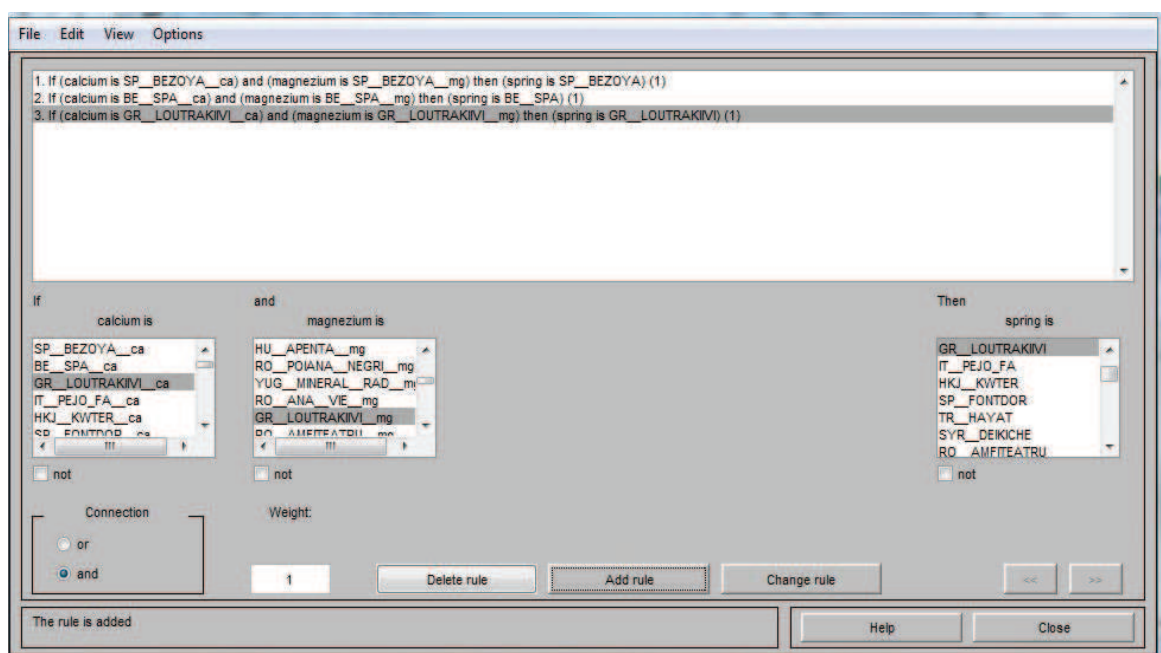


Fig. 6. Implementing the inference (rule set) for the fuzzy system in Matlab Fuzzy Toolbox

In order to check the functionality of the system, a pair of test values have been introduced, one for “calcium” and one for “magnesium”. It can be noticed that the Mg test value is common for two springs (having a different membership degree for each one of the two “springs”); the spring (or the springs) that correspond, as a result of the inference, to the test values, will be considered a solution. In the case in which there are several springs that accomplish the conditions specified by the user, those specific springs will be indicated on column

number 3; each potential solution will be coloured proportionally with the membership degree of the corresponding input values. Fig. 8 offers a graphical representation of the rules, as well as the input test values that have been introduced (left corner); the test values are (40; 7.8), pertaining to the spring Font-Vella Girona from Spain; the third row, „spring,” matches this value, thus, the corresponding spring (number 9) is highlighted with blue colour (see row). Fig. 9 shows a close-up of the rules.

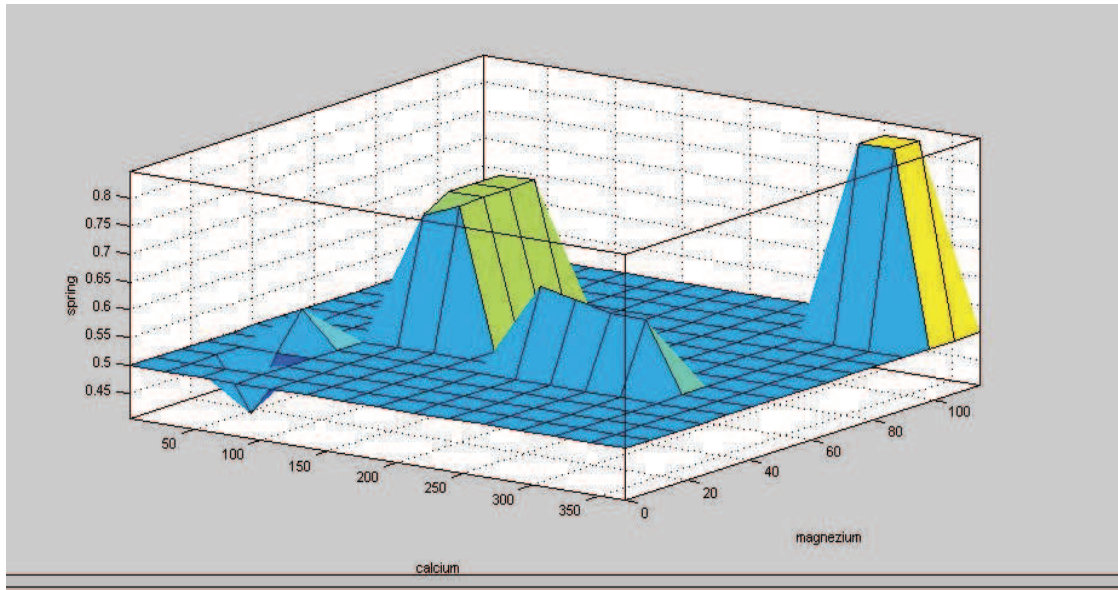


Fig. 7. Surface-type graphical representation of the fuzzy system

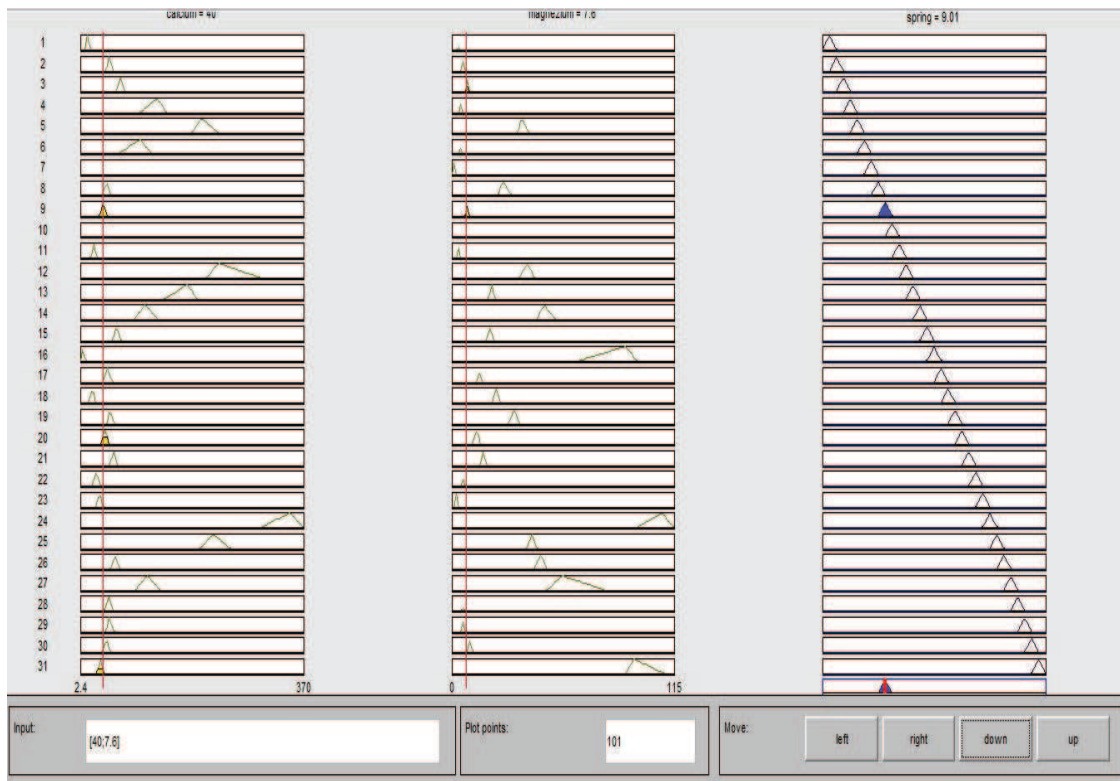


Fig. 8. Graphical representation of the rules

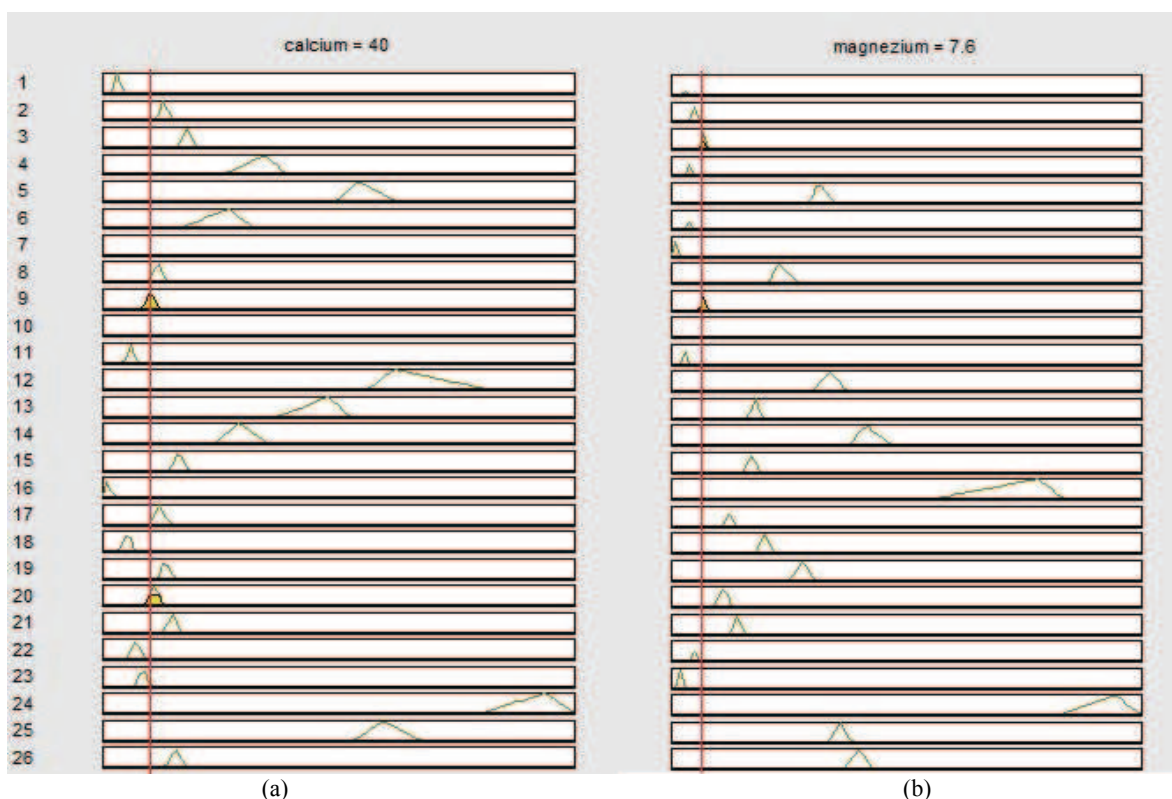


Fig. 9. (a) Graphical representation of the membership functions for the input variable “calcium”
(b) Graphical representation of the membership functions for the input variable “magnesium”;
when applying viable test values; two results matched for each input, with different matching degrees

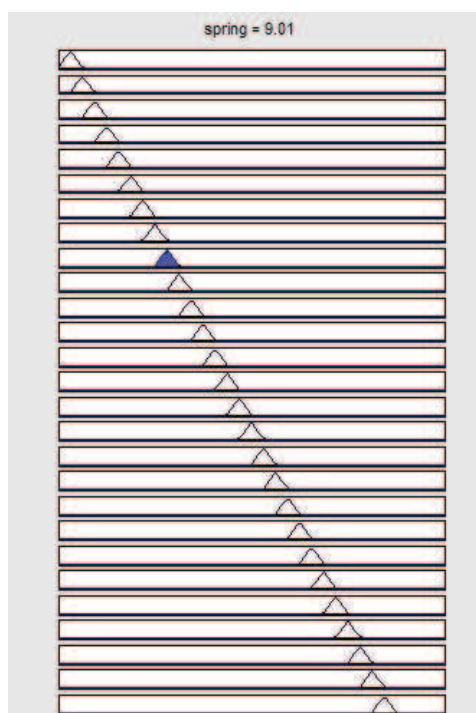


Fig. 10. Results of the output variable “spring” when applying viable test values

The answer (answers) can also be visualized in the Matlab command window with the following command line:

```
>> Name_of_the_fuzzysistem.output.mf(1,9)
```

where 9 stands for the number of the spring, as indicated by Fig. 10. The output line is thus:

```
ans =  
    name: 'SP_FVGIRONA'  
    type: 'trimf'  
    params: [8 9 10]
```

5. Conclusions

The method implemented in this project offers the advantage of reducing the number of analyzed components (anions and cations), when identifying the source of an unknown mineral water sample. Although the system has its limitations (e.g. the intervals of the membership functions are not uniform), it has the advantage of offering acceptable solutions; furthermore, it illustrates a global image of the system, a representation that allows a better understanding and interpretation of the result.

The field of computational intelligence has a clearly defined set of advantages: it optimizes the parameters with high-complexity objective function surfaces, offering a set of potential solutions (Topcu, Karacasu and Uygunoglu, 2014).

This article, through its purposes, has an interdisciplinary character, its results regarding the pharmaceutical domain, as well as the field of artificial intelligence. Due to the mathematical approach, as well as the applicability of the results, the project has a significant impact in the medical and chemical domains, seeking to identify a new

method of investigative analysis of mineral waters, which offers a high degree of precision and less expenses than traditional methods.

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REASONS FOR NON-PARTICIPATION IN RECYCLING OF SOLID WASTE IN NORTHERN MALAYSIA: A CASE STUDY

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Abstract

It is widely accepted that public support is vital to the success of most recycling programmes. The actions of householders are paramount to the success of any sustainable waste management policies whether local, regional or national. This paper presents a study of householders' attitudes to recycling of solid wastes in Malaysia, which supports the idea that careful planning and design are critical for the success of a new recycling programme. A postal questionnaire survey was administered to households in Penang state located in north Malaysia. Quantitative analysis of the 417 responses focused on reasons for non-participation in current recycling schemes. Statistical analysis showed that many householders refrain from recycling because of their negative perceptions of the distance to the recycling points and the lack of recycling facilities in their neighbourhood.

Key words: attitudes of householders, Northern Malaysia, Penang state, recycling, solid waste, survey

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1. Introduction

Recycling is a process in which used materials are collected, broken down and converted into new products. Effective waste recycling from domestic waste is not possible without deep involvement of public and householders. Thus, in order to support the design, development, and delivery of recycling schemes it is important to understand who the non-recyclers are, why they do not recycle, and what factors prevent them from recycling.

Malaysia generates approximately 18,000 tonnes of solid waste daily, of which only 70% is collected and disposed of by local authorities (Abdelnaser, 2008). The remaining 30% is either disposed illegally or is recycled informally. As usual, these circumstances are partly due to the general apathy of the public towards proper waste disposal and in part the lack of a proper policy on

solid waste management from national, regional and local governments. In fact, there is a real need to educate the public on the profound ramifications accruing from improper disposal of solid waste – including negative impacts on public health, the environment and the economy. Such educational initiatives should focus on changing attitudes amongst the local population so that recycling initiatives should be embraced, supported, applied and developed.

In the view of the foregoing facts, this study attempts to identify the possible and beneficial upcoming attitudes of householders with regard to recycling solid waste as well as evaluate current recycling campaign practices and intensity levels in the east coast and northern regions of Malaysia. The key aim of the research is to gain an insight into the reasons for non-participation of the general populace in recycling initiatives.

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In Malaysia, collection of recyclable materials is carried out by both the full-time disposal site scavengers and the municipal waste management teams who compete for the quality materials, which will derive an income. The money earned from scavenging the recyclable waste material provides additional income to the municipal collection crews who will defend their territory from other scavengers. As the crews have easier access to recyclable materials generated from households than disposal site scavengers, the recyclable materials they collect have higher values and are a significant revenue-source for the crews (Abdelnaser, 2008).

Despite the relative lack of success and receptivity to the concept of planned recycling by the public, the government has initiated several measures to improve the image of recycling amongst the general public (Abdelnaser, 2008). For instance, in order to consolidate the role recycling plays as a cornerstone in waste management policy initiatives, the Malaysian government has promulgated a new law on solid waste management in addition to drafting a Strategic Plan for Solid Waste Management in Malaysia (Abdelnaser, 2008; Ong, 2006; Zulkifli, 2007). According to this plan, the principal management options are considered as a hierarchy of integrated waste management policies including waste minimization, reuse, material recycling, energy recovery and landfill. The Bill, which is part of the National Solid Waste Management Policy, was approved by Cabinet at its meeting on 16 September, 2006.

Ong (2006) stipulated that this was “part of the government’s continuous measures to work out, among others, appropriate incentives besides instituting new regulations to promote recycling in the country”. The Bill finally passed in January 2007. In fact, two important bills related to solid waste were adopted by the Ministry of Housing and Local Government in 2007. The first was the Solid Waste and Public Cleaning Management Bill 2007, and the other was the Solid Waste and Public Management Corporation Bill 2007 (Zulkifli, 2007).

Ong (2006) hailed the passing of the Bills as “landmark decisions which would help create a systematic solid waste management programme throughout the country”. The Bills required the setting-up of a National Solid Waste Management Department as the regulatory body and the Solid Waste Management Corporation to conduct waste management operations and service delivery. In fact, the Bill got approval from Cabinet on 2 July 2007. By 30th August 2007 the Bill was passed and must be enforced from 1st April 2008. Today recycling is receiving increasing attention as the nation struggles with the problems caused by Municipal Solid Waste (MSW).

In fact, quadrupling the recycling effort is a key goal for many state and local governments, private companies, and public interest groups as current methods of solid waste management have been hindered by financial, spatial and technological

constraints (Abdelnaser et al., 2007). The time is therefore right to assess what progress has been made and what barriers exist to the development of more successful recycling programmes in Malaysia. This study was undertaken in the hope that it may aid in the development of recommendations that the governmental officials could choose to adopt to further encourage the development of recycling practices in Penang State. This should also enable the Government and other authorities in Malaysia to develop an information base, which is currently lacking and is a prerequisite for exploring the possibilities for future applications and changes in the system.

2. Literature review

2.1. Profile of the reasons for being a recycler and non-recycler

Different disciplines ranging from Psychology to Sociology to Economics to Law have devoted studies to the recycling issue, having a common goal i.e. determining what factors affect recycling participation. Generally it is evident a large discrepancy in claimed recycling attitudes to actual recycling behaviors in people, since there is more public chatter and declared support for recycling, but less public participation in recycling. Researchers have found a number of key reasons for these discrepancies. First, the lack of accessibility to an effective recycling infrastructure that enables householders to recycle their waste is clearly a crucial part of any recycling programs failure (Martin et al., 2006), but there are many other factors which motivate householders to make use of that infrastructure (Abdelnaser et al., 2007; Abdelnaser, 2008; Abdelnaser and Read, 2008).

Given that household waste recycling in Malaysia is largely a voluntary activity, understanding these other motivational factors is essential if the practice of recycling is ever to attain its full potential and become a part of everyday household routine. Price (2001) stated the role of the local authority and actions of the householder as being essential for the success of sustainable waste policies. However, understanding households’ reasons for not recycling is an important indicator to improve participation in recycling of solid waste. Perrin and Barton (2001) noted again that the key link in increasing recycling rates is the household.

The understanding of the public attitudes towards buying products made from recycled materials is therefore necessary. Meanwhile, Thomas (2001) agreed that public participation is critical to the success of recycling and also stress the importance of how well that participation is performed. Price (2001) reported that a survey in South Bedfordshire, England revealed that 83% of respondents claimed to do recycling, but a survey of actual participation showed that at best only 50% were doing so on a regular basis with the recycling

rate for the area being only 3%. It would appear that participation was indeed quite lower. When Perrin and Barton (2001) studied participation in a kerbside scheme in Leeds, England, it was shown that 98% of people surveyed before the scheme was implemented, claimed that they would use it, but only half actually did. Similar results were obtained by Williams and Kelly (2003) where actual participation in a recycling scheme in Wyre was found to be only about half of what had been claimed by the potential users. Chan (1998) studied the psychology of recycling behaviour in Hong Kong and found that whilst there was a high correlation between people's attitude and their intention, the correlation dropped when compared with actual behaviour.

Perrin and Barton's (2001) survey of two kerbside schemes found that the commonest reasons given for not recycling before the implementation of the schemes were the lack of time, distance to centres and storage/ handling problems. Most probably the kerbside schemes would hinder or at least mitigate most of these reasons, but when Perrin and Barton studied the participation levels after the implementation of recycling, it was found that with one of the schemes participation was only half that expected. McDonald and Ball (1998), and Williams and Kelly (2003) identified a perceived insufficiency of recyclables as being the main reason for non-participation in the kerbside schemes. McDonald and Ball (1998) speculated that the large size of the scheme's bins might have tended to dwarf small amounts of material, rendering it insufficient in the eyes of the householder. In this particular case though, the material in question was paper, which could easily have been accumulated in the bin until the householder's threshold for a sufficient load had been exceeded.

Coggins (1994) noted that 35% of non-recyclers in a survey in Sheffield cited inconvenience and a lack of facilities as the main barriers to their participation, with "nothing to recycle" being much less important. A survey into the British public's attitudes to the environment by DEFRA (2002) found that the most likely reason for not recycling was the inadequacy of local facilities, followed by the facilities being too far away and a lack of storage space at home. The effort required in recycling was cited by Burnley and Parfitt (2002) survey as the most common reason for not recycling, and that access to better facilities would encourage more non-recyclers to participate. Belton et al., (1994) found that the average distance in Glasgow to collection center is 0.64 km for pedestrians (39% cases) and 1.53 km for car users (59%). Similarly, Ball and Lawson (1990) reported figures in their study which showed that only 27% of people walked to the disposal point and most (71%) used a car. On the contrary, Powell et al. (1996) obtained an average of 3.66 km, while Butler and Hooper (2000) proposed a limit of 1 km as the distance that a typical citizen could cover by car or walking.

Robinson and Read (2005) found that a contributing factor for those who were not recycling was a high lack of awareness of the location of the nearest facility. Meanwhile, González-Torre and Adenso-Díaz (2005) commented that when citizens who are environmentally concerned have bins near to their home, they appear to be willing to recycle more fractions than when they have to walk for a longer distance to drop off the waste, due to the inconvenience of carrying the large volumes that this type of waste usually occupies. It was concluded that distance and access to the bins were obviously an incentive to recycling. Therefore, a citizen's attitudes depend on the knowledge about a facility (Rahardyan et al., 2004). In the UK, the Environment Agency (DEFRA, 2002) study identified a lack of time as the barrier to recycling for 28% of non-recyclers, although other reasons for non-participation were not sought. Three-quarters surveyed by MORI (2002) assumed they would recycle more if they had access to a kerbside scheme; nevertheless, the same survey also found that around half of the people who had access to such a scheme were unaware of it.

The profile of recyclers and their reasons for doing so might be expected to be the opposite to those of the non-recyclers. Martin et al., (2006) conducted a study on social, cultural and structural influences on household waste recycling in the Borough of Burnley, England, and they found that householders are very willing to participate in recycling as shown by almost 80% claiming to recycle paper, but that local recycling services are too unreliable and inconvenient to allow them to do so comprehensively. Although a large literature has discussed the factors influencing recycling behaviour and attitude in solid household waste management, there is little achievement to the recycling of solid waste in practice, especially in less developed countries. Apparently, in reviewing the available literatures, it becomes clear that there are many possible factors that may influence recycling actions and help non-recyclers become recyclers.

2.2. Economic incentives and rewards

In this respect, Foxall (1995) suggested that to encourage non-participants to get involved in recycling, incentives should be offered to initiate the desired recycling behaviour. He found that while prompts and educational materials have minimal effects on behaviour, the provision of hedonic reinforcers (e.g. prizes) has a substantial effect. Noehammer and Byer (1997) concluded that the participation rate is positively affected by economic incentives, though they acknowledged that the literature generally links increased participation to paying for disposal. Hong (1999), reporting on the implementation of a unit-pricing system for waste disposal in Korea, found that after adoption of the scheme, waste generation was reduced by nearly 18% and recycling, which was provided free of charge, was up by nearly 27%.

However, unit pricing frequently led to an increase in fly tipping and illegal burning, and volume-based systems may be less effective at promoting recycling than weight-based ones, because of the opportunity to compact all waste into the general waste bin at home (Martin et al., 2006). A study performed by Chung and Poon (1994) revealed that in Hong Kong the less well-off were more responsive to charging and so recycled more than the more affluent who could more easily afford to pay for waste disposal rather than adopt recycling. Barr et al., (2001) proposed that individuals either always or never recycle, thus any incentive to encourage trials of recycling schemes has to sustain the new behaviour of the novice recyclers until their recycling becomes the norm.

The general conclusion from a review of these studies is that with the provision of convenient, visible recycling campaigns and a successful scheme involving clear information for participants and possibly rewards of some kind; non-recyclers will become recyclers. Perrin and Barton (2001) noted that the introduction of a kerbside scheme for all recyclable materials significantly raised the proportion of households who claimed to participate in the scheme.

2.3. How to motivate non-recyclers?

The motivational factors behind recycling behaviour have been heavily researched in several studies, which have sought to isolate specific traits that can be attributed to recycling in participation. The research by Bratt (1999) emphasized the need to understand the influences of consumer environmental behaviour and to identify variables that predicted such behaviour. The study concluded that the social norm, which is the consistent behavioural patterns of a majority of individuals surrounding the individual, provided no link to behaviour. It was striking, though, to note that in the findings of Gamba and Oskamp (1994), they identified peer pressure, as an important predictor or motivational factor of recycling behaviour. This means that when in the presence of others, the subjects were inclined to make more socially responsible decisions, especially when peers actually recycled. Garcés et al., (2002) noted that environmental awareness and knowledge of the environmental impact of urban waste were factors that did seem to determine an individual's recycling behaviour.

Looking at more previous research, there are many studies carried out in different regions and countries. The key motive in recycling as pointed out by numerous researchers is knowledge (Hornik et al., 1995). They decided that the only way to instill recycling habits in people is through education and awareness building. Previously, numerous studies showed that if households' participation needs to be increased, then there is a need to continue to reinforce the motivation to recycle. To achieve this, it is important to know more about how recyclers are

motivated and also to know which factors motivate non-recyclers. McDonald and Ball (1998) explored some important reasons for non-users not recycling plastic in Glasgow, the two most important being no local facilities and inconvenience. These reasons were almost similar to what Grodzińska-Jurczak et al. (2006) found when they conducted a study on the effects of an educational campaign on public environmental attitudes and behaviour in Poland. However, their key findings were that local facilities, services and locations were very poor, which led to the design and delivery of a targeted education campaign to correct perceptions and attitudes.

In contrast, Perrin and Barton (2001) conducted a related study and they found the most important factor to influence recycling in a kerbside recycling scheme was good facilities which were nearby and convenient. Most of these studies are from developed economy locations. This study has utilized this previous research in designing the research programme described here, but has adopted the surveys etc. to reflect more closely the issues facing the Penang state.

3. The study area

Penang is the one of the 13 States of the Federation of Malaysia. It is located in the northern part of Malaysia (Fig. 1) and is bounded on the north and east by the State of Kedah, to the south by the State of Perak and to the west by the Straits of Malacca and Sumatra (Indonesia). Penang consists of the Island of Penang (covering an area of 285km²) and a costal strip on the mainland known as Province Wellesley. It has a population of about 1 million people (Abdelnaser et al., 2007). The Island and the Mainland are linked by the 13.7 km long Penang Bridge (Fig. 2).

The Executive Council is the highest administrative body in the State, whilst at the local government level, the State is divided into 2 local authorities, one on the Island and the other on the Mainland, namely the Municipal Council of Penang Island (or Majlis Perbandaran Pulau Pinang (MPPP) in the local language) and Province Wellesley (or Municipal Council of Seberang Perai (MCSP)) respectively.



Fig. 1. Penang State (red circle) and Malaysia



Fig. 2. Map of Penang State (Green colour)

4. Research methodology

The survey utilized a standardized questionnaire and pre-tests were conducted in order to ensure item clarity and non-ambiguity. The research instruments were fully utilized on 750 randomly selected households in Penang State. Data were collected between January and March 2007.

The questionnaires were distributed manually from house by house and the households were explained what the research was looking at and how to answer the questionnaires. Follow-up visits were made to check the feedback with the households. The respondents were given prepaid envelopes and asked to return them within a three months timeframe. Of the 750 questionnaires sent out in Penang State, 417 questionnaires were returned.

Thus, the return ratio was 56%, representing a highly satisfactory level of participation when compared to similar postal surveys (Hansmann et al., 2006). All data were analyzed using the Statistical Package for Social Science (SPSS); Version 17.0 for Windows software. The alpha level was set at 0.05 to determine statistical significance, and a descriptive statistics with a number of tests were used including, Chi-square tests.

4.1. Conceptual framework of the study

The purpose of the study is to Reasons for non-participation in recycling of solid waste in northern Malaysia. Two recycling campaigns were launched by the Ministry of Housing and Local Government (MHLG), the first in 1993 and the second in 2000. Both campaigns did not get positive response due to the lack of response from the Malaysian public. No study has been done to investigate the reasons why the recycling program or even the campaigns were not successful. This prompted the researcher to carry out this study.

This research is basically an experimental research where it is to determine and investigate the cause and effect relationships between the dependent and independent variables. In this theoretical framework, factors for non-participation such as lack of awareness and knowledge on either recycling solid waste or its tow conducted campaigns are

independent variables and recycling of solid wastes programme is a dependent variable as illustrated in Fig. 3.

4.2. Socio-demographic characteristics of respondents in Penang State

In Penang 417 respondents participated. Seven demographic variables measured, namely, race, age, gender, educational level, occupation, income level and house type. The relevant demographic details are presented in Tables 1 and 2.

Table 1. Distribution of respondents according to ethnicity, age, gender and education level

Demographic	Respondent no. and percentage
Ethnicity	
Malay	154 (37%)
Chinese	218 (53%)
Indian	45 (10%)
Age	
Under 26 years old	220 (52.8%)
26-34 years old	59 (14.1%)
35-44 years	50 (12%)
45-54 years	64 (15.3%)
55-59 years	20 (4.8%)
60 years or over	4 (1%)
Gender	
Male	219 (52.3%)
Female	199 (47.7%)
Education level	
Did not attend any school	2 (0.5%)
Primary School	282 (67.6%)
College	25 (6%)
University	108 (25.9%)

Table 2. Distribution of respondents based on occupation, income level and housing type

Demographic	Respondent no. and percentage
Occupation	
Government	93 (22.3%)
Private	45 (10.8%)
Own Business	85 (20.4%)
Housewife	43 (10.3%)
Student	151 (36.2%)
Income level	
Did not have any income	107 (25.7%)
Less than RM499	71 (17%)
RM 500 to RM 999	30 (7.2%)
RM 1000 to RM 1999	48 (11.5%)
RM 2000 to RM 2999	62 (15%)
RM 3000 to RM 3999	45 (10.6%)
RM 4000 to RM 4999	35 (8.4%)
RM 5000 and above	19 (4.6%)
Housing type	
Semi-Detached	35 (8.4%)
Bungalow	17 (4%)
Single- Storey Terrace	62 (15%)
Double- Storey Terrace	62 (15%)
Shop House	9 (2.2%)
Flat	97 (23.2%)
Condominium / Apartment	118 (28.2%)
Village	17 (4%)

1 US Dollar = RM 3.12 (October 2010)

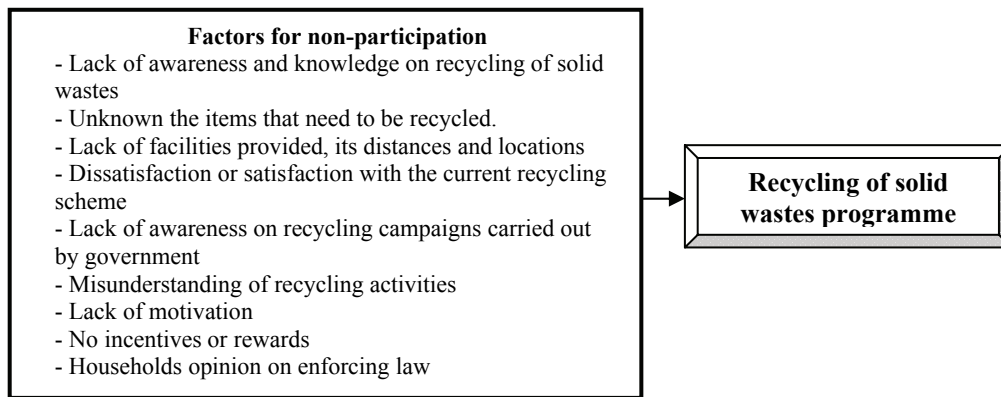


Fig. 3. Conceptual framework of the study

5. Results

5.1. The current involvement in recycling of municipal solid wastes

As shown in Fig. 4, 62.4% of respondents in Penang are currently involved in recycling.

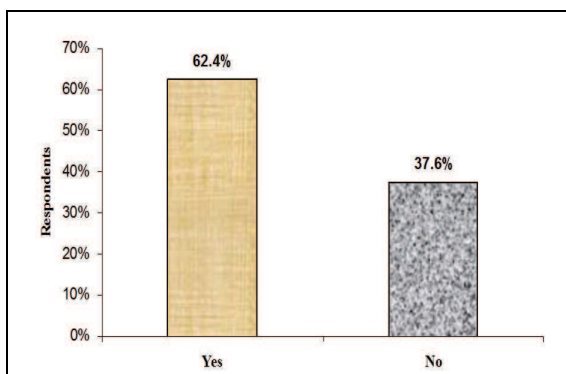


Fig. 4. Current involvement in municipal solid waste recycling

Respondents were asked to encircle all their reason (s) for recycling. Overall, 46% of the respondents recycle to save landfill space, whereas 54.9% recycle to protect the future environment/generation (Table 3). The survey results indicate that newspapers, followed by magazines, are the most commonly recycled materials in Penang.

Other paper materials, such as cardboards, are also some of the most recycled materials identified by Penang residents. Very few (7.9%) recycle leaves and yard wastes (Table 4). Of 417 respondents, 25.2% do not participate in recycling activities.

From this number, 30.9% indicate inconvenience/no time as the primary reason for not recycling (Table 5).

5.2. Facilities provided

Four questions were used to check respondent attitudes toward the recycling facilities provided by the government of Penang. In several locations, local authorities have placed bins and containers in which

households may deposit their recyclables. Respondents were asked if they ever saw these recycling centres in their areas.

Table 3. Reasons for recycling municipal solid wastes in Penang

Description of recycling reasons	Percentage of respondents
1. Good facilities provided / convenient	30.2%
2. To protect future environment / generations	54.9%
3. Saves landfill space	46%
4. Personal satisfaction / habit	42.7%
5. Saves dustbin space	21.3%
6. Peer pressure	7.4%
7. Incentives/ monetary reward	24%
8. Awareness about the importance of recycling / duty	49.2%

Table 4. Materials recycled by Penang residents

Materials recycled	Percentage of respondents
1. Newspapers	62.6%
2. Magazines	54.9%
3. Other paper or cardboard	48%
4. Textiles	9.8%
5. Glass Jars	12%
6. Drink Cans (aluminum or tin)	42%
7. Food cans	29.3%
8. Plastic Containers	16.1%
9. Plastic Bottles	31.2%
10. Plastic Carrier Bags	20.6%
11. Leaf / yard waste	7.9%

The chi-square analysis reveals that awareness of these recycling centres is significantly related to race, age, gender, occupation, and income (Table 6). As shown in Fig. 5, 41.2% of the non-recyclers know the location of the nearest collection points, whereas 70.5% assert that these points are not easily accessible and are unsuitably located. This explains the phenomenon of illegal dumping in Penang (Fig. 6).

In terms of distance, only 12% of the respondents indicate that their designated collection sites are within one kilometre away from their

homes, whereas 13.4% indicate that such sites are farther than five kilometres away from their homes.

Table 5. Reasons for not recycling in Penang

<i>Reasons for non-recycling</i>	<i>Percentage of respondents</i>
1. Inconvenience / no time	25.2%
2. Facilities too far away / inadequate	30.9%
3. Not interested	9.4%
4. No reward / money	5%
5. Do not like the recycling bin	1.9%
6. Have to put the bin outside the pavement	1.7%
7. Forget to leave the bin out	3.6%
8. I do not understand what to do	2.6%
9. Lack of information or insufficient knowledge	10.8%
10. Storage / handling problems	11%
11. Never really thought about it	7%
12. Not enough materials to recycle	6.5%
12. Too much effort needed	10.3%
13. Waste time	3.4%
14. My bin is not always collected	5.5%
15. Do not bother	2.4%
16. Believe there are better ways to handle my garbage	4.1%

Table 6. Level of significance of respondent opinions on the location of recycling centres based on demographic factors

<i>Demographic</i>	<i>Chi-square results</i>	
	χ^2	<i>P-value</i>
Race	19.6	0.003 ***
Age	39.3	<0.001 ***
Gender	6.8	0.033 *
Education level	12.7	0.392
Occupation	50.4	<0.001 ***
Income level	50.3	<0.001 ***
House type	22.3	0.073

*** = statistically significant at $p < 0.001$

** = statistically significant at $p < 0.01$

* = statistically significant at $p < 0.05$

Furthermore, the results show that a large proportion of Penang residents (60.2%) do not have any idea about the distance between the location of collection sites and their homes (Table 7). Respondents were asked about the frequency of their recycling activities. In all, 29% prefer to recycle weekly, whereas 41% only recycle when necessary (Table 8).

Furthermore, non-recyclers were asked how much time they would be willing to spend to reach a recycling centre. The results reveal that 42.2% are willing to spend less than 10 minutes of walking to reach a recycling centre, whereas 22.1% are not at all likely to go to any recycling centre. Less than 10% are willing to spend 10 minutes, 16–20 minutes, and 20 minutes or above for travelling to a recycling centre (Table 9).

Non-recyclers were also asked for their views regarding the appropriate location for recycling drop-off centres. For 50.8% of the respondents, the most

suitable and convenient location for drop-off centres would be 'anywhere' (Table 10).

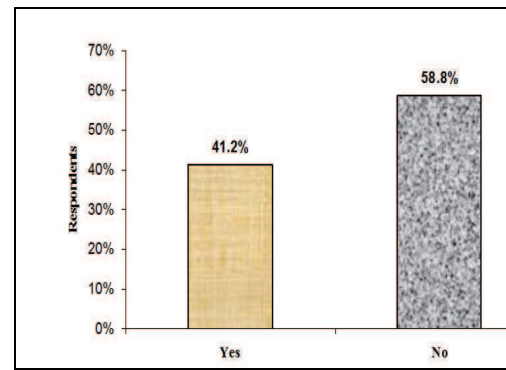


Fig. 5. Percentage of respondents who know the location of the nearest recycling points

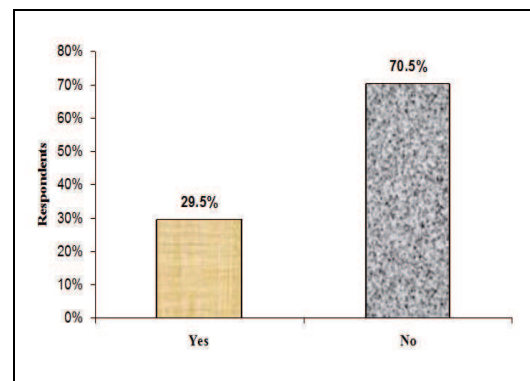


Fig. 6. Household knowledge on the accessibility of the collection points recycling facilities

Table 7. Respondents' opinions about real distance to the local collection points

<i>Available distances</i>	<i>Percentage of respondents</i>
1. Within 1 Km/radius	12%
2. Within 2-3 Km/radius	8.9%
3. Within 4-5 Km/radius	5.5%
4. More than 5 Km	13.4%
5. Do not know at all where collection point is	60.2%

Meanwhile, 19.7% of the respondents agree with the establishment of 'centrally located special areas dedicated to recycling'.

Table 8. Respondents' opinions about the most suitable frequency for their recycling collection

<i>Items</i>	<i>Percentage of respondents</i>
1. Every day	5.8%
2. Every 2 days	0.7%
3. Every 3 days	2.2%
4. Every week	29%
5. Every 2 weeks	5.3%
6. Every month	14.6%
7. Every three months	1.4%
8. When it is necessary	41%

Table 9. Acceptable travel time for non-recycler to reach the nearest recycling centre

<i>Items</i>	<i>Percentage of respondents</i>
1. Less than 10 min	42.2%
2. 10 min	7.9%
3. 11-15 min	11.8%
4. 16-20 min	7.4%
5. 20 min and above	8.6%
6. Not likely to go to recycling centers	22.1%

Table 10. Most convenient locations for recycling drop-off centres

<i>Items</i>	<i>Percentage of respondents</i>
1. Fire or police station	0.7%
2. Shopping area or grocery store	14.9%
3. Park or recreation area	7.4%
4. Centrally located special area dedicated to recycling	19.7%
5. Petrol station	6.5%
6. Anywhere	50.8%

Concerning the question on “how much extra money they would be willing to ‘pay’ for their monthly waste collection bill for a regular kerbside recycling scheme”, it was found that, a large proportion of the respondents are reluctant to pay any amount for monthly waste collection under a regular kerbside recycling scheme. Meanwhile, 22.5% are willing to pay an extra RM1–2 (Table 11).

Table 11. Willingness to incur extra monthly costs for waste collection under a kerbside recycling scheme

<i>Items</i>	<i>Percentage of respondents</i>
1. Less than RM 1	15.1%
2. RM1 – RM 2	22.5%
3. RM 3 – RM 5	21.6%
4. RM 6 – RM 10	3.8%
5. RM 10 and above	3.1%
6. Would not be willing to pay	33.8%

6. Discussion

6.1. The current involvement in recycling of municipal solid wastes

Households were asked about their current involvement in the recycling of household solid wastes. We found that 37.6% of the respondents are not currently involved. Non-participants were asked for their reasons behind non-participation. For the majority of non-participants (25.2% of the respondents), recycling is inconvenient or they have no time for recycling.

Waste Watch (1999) had the same finding in the United Kingdom; the main reasons for not recycling are inconvenience (19%) and laziness (30%). Similar findings were also reported by Darby and Obara (2005), and Thomas (2001). In the present

case study, the second important reason behind non-participation is the lack of suitable facilities. For most of the respondents (30.9%), the facilities are too far from their houses and are even inadequate in some areas. Interestingly, Waste Watch also found in 1999 that some households (12% of the respondents) complain about the inadequacy of local facilities. This finding is also found in other studies (e.g., Darby and Obara, 2005; Perrin and Barton, 2001; Read, 1998, 1999; Salhofer and Isaa, 2002; Thomas, 2001).

These studies found that the inadequacy of local facilities is a significant barrier to recycling. Some experts have noted that acceptance plays an important role when locating SWM facilities in available locations (Joos et al., 1999). The other reasons for non-recycling include wasting time, and irregular recyclable collection.

6.2. Facilities provided

Households were also asked about the provision of recycling facilities. A large percentage of the households do not know the location of the nearest collection points in their areas. Almost all of those who responded to the survey claim that they have seen recycling bins at one time or another. Unfortunately, only a small proportion of the respondents have actually used the recycling bins because according to 70.2% of them, these bins are not easily accessible. This result concurs with the finding of González-Torre and Adenso-Díaz (2005).

Research has shown that when environmentally concerned citizens have bins near their homes, they appear to be more willing to recycle more than when they have to walk a long distance to drop-off points. In terms of distance, the majority of Penang households do not know where the recycling facilities are located. However, a large percentage of the respondents in the study area have indicated that if the recycling sites are within one kilometre away from their houses, they are likely to use them. This is similar to the findings of Butler and Hooper (2000) who proposed a limit of one kilometre as the distance that a typical citizen could cover by car or foot to use a recycling facility.

Only a few of the households (5.5% of the total respondents) are within a radius of four kilometres from the nearest recycling facility. Clearly, this suggests that distance is a significant barrier to the utilisation of recycling sites. Nixon and Saphores (2007) found that respondents living more than five kilometres away from the nearest drop-off recycling facility or those who see a limited role in environmental protection do not tend to support the recycling scheme. Undoubtedly, the farther the location of the collection points, the more discouraged households would be. Similarly, Butler and Hooper (2000) concluded that there is a direct and positive relationship between distance and the number of individuals who walk to collection points, that is, more people travel shorter distances.

Furthermore, individuals are willing to walk farther distances if the trip can be used for other purposes, such as for shopping or going to work. Foo (1997) found that the placement of additional recycling bins increases recycling participation, and González-Torre and Adenso-Díaz (2005) commented that when environmentally concerned citizens have bins near their homes, they appear to be willing to recycle more than when they have to walk for a long time to drop off their wastes. Moreover, Robinson and Read (2005) found that a high lack of awareness of the location of the nearest recycling facility contributes to non-recycling. Thus, it can be concluded that a short distance and suitable access to bins promote recycling.

A recent study by Vicente and Reis (2007) found that the placement of additional bins increases recycling participation. The benefits that recycling facilities may bring to local residents can influence attitudes toward recycling (Foo, 1997; Tonglet et al., 2004; Williams and Kelly, 2003). Moreover, household attitudes depend on household knowledge about the adequate provision of recycling facilities (Rahardyan et al., 2004; Vicente and Reis, 2007). In Penang, most of the respondents are unwilling to pay for kerbside recycling because the current cost is deemed too expensive. Instead, they are willing to pay only within the range of RM1–2 or RM3–5. Kum et al., (2005) proved that solid waste collection and recycling is a very costly service and is the most expensive phase of waste management; the same holds true for Malaysia.

However, in areas with semi-detached, single-storey, and two-storey houses, a study has shown that residents are willing to pay an extra fee ranging from RM3 to 5. Perhaps, people in these areas have a better appreciation of the surrounding environment or they may be relatively richer compared with their neighbours. Huang et al., (2006) found that most Ningbo residents in China are willing to pay for local environmental improvements. In contrast, in this present case, respondents are willing to pay only if the fee is less than RM1. Penang residents may not be financially capable, or they may be unwilling to pay for extra fees as far as results in their areas are not encouraging. In other words, considering that most of the respondents earn RM499 a month or have no income (25.7% being students with no income), they may not be financially capable of paying recycling fees. Hence, income is one of the key factors affecting household acceptance or willingness to pay for extra recycling fees. In this regard, Chung and Poon (1999) found that the share of family income rather than the absolute level of charge largely affects household acceptance of the rate of recycling charge in the two lowest income groups.

The majority of respondents only recycle when necessary due to a lack of time to recycle more often or a general laziness to do so. However, many respondents consider that weekly recycling is desirable. The weekly collection of recyclables is preferred because it is practical and convenient. This

finding is supported by Grodzińska-Jurczak et al. (2003) who found that households agree with weekly collection and recycling in the City of Jaslo in Poland because of convenience. Moreover, Martin et al. (2006) found that weekly recycling is preferred by 70% of UK residents.

In the present study, only a few of the respondents recycle less often (i.e., every month) because of a number of reasons: they have busy schedules, they generate less recyclables, or they have agents who deal with recyclables. Surprisingly, some of the households prefer to recycle daily, probably because they feel disgusted with the current situation of solid waste management in the area; there is extensive fly-tipping and open dumping in the city. According to the respondents, to enhance recycling efficiency, recycling centres should be located closer to residential areas. This location strategy will undoubtedly play an important role in encouraging the development and implementation of additional recycling activities in the case study locations. According to Belton et al., (1994), one of the reasons for non-participation in recycling centres in Glasgow is a perception that the centres are too far away. A similar survey on recycling by McDonald and Ball (1998) found that the chief reason for not recycling is the lack of local facilities, although the survey was conducted next to local recycling centres. Furthermore, Tonglet et al., (2004) suggested that pro-recycling attitudes are the major contributors to recycling behaviour, and these attitudes are influenced by the provision of appropriate recycling opportunities, facilities, and knowledge.

These results are also supported by Robinson and Read (2005) who found that a high lack of awareness of the location of the nearest recycling facilities contributes to non-recycling. If one of the strategies to encourage residents to take their recyclables to centres is by locating these centres closer to houses, then the Ministry of Housing and Local Government (MHLG) and Municipal Councils (MCs) must also consider how to communicate this positive message effectively to residents. Effective communication will overcome the problem of perceived distance and time. Meanwhile, another preferred option is to pay for segregated recyclables (25.6%), which would further motivate participation. For the majority of Penang respondents (47.6%), the most acceptable time to be spent for going to and from a recycling centre is less than 10 minutes. Clearly, people are willing to recycle, but they yearn for more convenience.

Tonglet et al., (2004) suggested that pro-recycling attitudes are major contributors to recycling behaviour. Through these attitudes, people are not deterred by the physical issues of recycling (e.g., time, space, and inconvenience). Penang respondents prefer that facilities be located 'anywhere'; others suggest the establishment of 'centrally located special areas dedicated to recycling'. Many believe that locating recycling facilities 'anywhere' is the only effective way to attract and motivate households

to recycle. Hence, areas, such as shopping complexes, petrol stations, and even mini-markets, must have recycling facilities in the future; this will also minimise the throwing of wastes from buses and cars (Abdelnaser and Read, 2008).

If new facilities are located 'anywhere' and everywhere, then the active participation of residents will be higher than when a centralised location approach is adopted. This is consistent with numerous other studies (González-Torre and Adenso-Díaz, 2005; Tonglet et al., 2004; Vicente and Reis, 2007). It is not always desirable to provide drop-off centres in special areas dedicated to recycling because their use requires additional effort on the part of the public. Instead, a dispersed network of drop-off facilities across the whole city or town, which can easily be seen and accessed by households, would encourage recycling participation.

7. Conclusions

Recycling is a part of solid waste management approach that the States of Malaysia must seriously consider in the coming years to address the country's mounting waste management problem. However, a recycling programme is only successful if households support and actively participate in it.

In general, from the study of householder attitudes in the case study area there are a number of key reasons given by non-recyclers for their non-participation. It was obvious that a "lack of facilities" and the "distance to the facilities" were significant barriers.

Almost all the respondents in Penang state agreed that a weekly recycling collection would encourage them to recycle more, as would more local sites (less than 1km). The results outlined in this paper indicated that the majority of the households in the study area were willing to pay the range (1-2 RM) as extra monthly cost.

We expect that future central and local government policy makers listen to the commentary from these surveys and makes wise choices about the level, location and funding of future recycling programmes.

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CORRELATION ANALYSIS OF CH₄ EMISSIONS FROM PADDY SOILS WITH CHANGES IN OXIDIZABLE ORGANIC CARBON

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Abstract

Soil organic carbon is one of the key substrates affecting methane emissions in paddy fields. However, not all soil organic carbon forms methane. This study therefore involved comparative analysis of the methanogenesis of different organic carbon sources (rice straw, chicken manure and pig manure) in paddy field soils. The results indicated that whereas methane emissions from the pig manure treatment (PM) were not significantly different to those associated with the application of chemical fertilizer (CF), methane emissions from the chicken manure (CM) and straw treatments (RS) were greater by 1.67 times ($p < 0.05$) and 2.69 times ($p < 0.05$), respectively. Soil organic carbon content exhibited the same order as methane emissions: RS > CM > PM > no fertilizer. Correlation analysis revealed that, for different fractions of organic carbon, fraction 1 (organic carbon fraction oxidized by 33 mmol / L KMnO₄) and methane emissions were directly related. Thus, organic carbon in soil is easily oxidizable in organic carbon fraction 1 - the primary substrate for methanogenesis. The development of effective measures to reduce the content of this fraction may therefore represent a key method of mitigating methane emissions.

Key words: methane emission, organic carbon fraction, paddy field, soil organic carbon

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1. Introduction

Atmospheric methane (CH₄) is one of the most potent persistent greenhouse gases contributing to global warming (Cai et al., 2005; Manea et al., 2013). Global atmospheric CH₄ concentrations increased from a pre-industrial value of about 715 ppb to 1,732 ppb by the early 1990s. In 2005, CH₄ concentrations of 1,774 ppb led to a combined radiative forcing of 0.48 Wm⁻² (Forster et al., 2007). It is clear that the observed increase in methane concentrations is due to anthropogenic activities, predominantly agriculture and fossil fuel use (IPCC, 2007).

Paddy fields are considered important sources of atmospheric CH₄; according to the IPCC, 5 to 19% of overall estimated global CH₄ emissions originate

from rice paddies (IPCC, 2007). Numerous field- and model-based studies have focused on CH₄ dynamics in rice paddies, CH₄ emission being the research hot spot in greenhouse effect study.

Here the organic carbon decomposition through fermentive processes has been found to produce CH₄ in rice paddy soil. Although different researchers have produced contrasting results regarding the relationship between CH₄ emission and soil organic carbon (SOC) (Denier van der Gon and Neue, 1995; Wassmann et al., 1998), it maybe that the total carbon amount of CH₄ emission accounts for a very small proportion of the total soil organic carbon, it may be part of the organic carbon worked in CH₄ emission, the total SOC had not a directed relation with the CH₄ emission. Adoption of procedures that can extract the more labile fraction

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preferentially might be a more useful approach for the characterization of soil organic carbon resulting from different management practices.

Many researchers have found that labile organic carbon, which is sensitive to changes in environmental conditions, is the nutrition source available for heterotrophic growth of microorganisms (Janzen, 1987; Whitbread et al., 1998; Yakovchenko et al., 1998). As a result, its content in soil directly affects microbial activity (Bending et al., 2000; Haynes, 2005) which in turn influences the emission of CH_4 (Le Mer and Roger, 2001). Bujun and Samonte (1995) have argued that methanogens, microbial CH_4 producers, need additional available carbon for activation. Zeng et al. (2011) found the easily oxidizable organic carbon (EOC) in soil to be a good indicator of anaerobic carbon decomposition. EOC is classified as labile carbon compounds with the most rapid turnover rate.

Although a number of studies have examined variation in labile organic carbon under different soil management schemes, few have been carried out in terms of the relationship between labile carbon and CH_4 emission. A procedure based on the degree of oxidation of organic carbon (Blair et al., 1995) has been employed to fractionate carbon in terms of its lability, with the degree of oxidation under different concentrations of KMnO_4 (33, 167 and 333 mmol/L KMnO_4) used to determine individual soil carbon fractions. SOC could then be divided into three fractions according to their degree of oxidization (Blair et al., 1995).

Using the amount of organic carbon oxidizable by KMnO_4 as a measure of soil organic carbon lability, Chan et al. (2001) and Blair et al. (1995) identified considerable changes in the organic carbon fraction of soil after cultivation. The aim of the present study was therefore to investigate the dynamics of and relationship between labile OC and CH_4 emission, as well as to understand how labile OC affects CH_4 emission in paddy fields under different organic manure treatments. The produced results could then be applied to research aimed at alleviating CH_4 emissions.

2. Materials and methods

2.1. Study sites

The experimental field is located at Gansha Experimental Station in Hunan province, China (N $28^{\circ}08'18''$, E $113^{\circ}12'0''$). It is located in a typical rice production area in southern China, average annual precipitation is 1500 mm and the average annual temperature is 17.1°C . The soil for the experiment was derived from Quaternary red clay and was classified as a Fe-accumuli-Stagnic Anthrosol according to the Chinese soil classification system.

The basic soil properties before testing were: pH 6.6, soil organic carbon $19.3 \text{ g C}\cdot\text{kg}^{-1}$, total nitrogen $2.04 \text{ g}\cdot\text{kg}^{-1}$, available nitrogen $212.0 \text{ mg}\cdot\text{kg}^{-1}$,

available phosphorus $11.1 \text{ mg}\cdot\text{kg}^{-1}$, available potassium $97.0 \text{ mg}\cdot\text{kg}^{-1}$.

2.2. Treatments

The field experiments were started in 2010 at a site with a history of more than 100 years of rice cultivation. Work at our field experiment started in July 2011. Plots of $3.0 \text{ m}\times 2.8 \text{ m}$ in size under different fertilizer treatments were arranged in a completely randomized block design with three replicates each.

The experiment was designed with the following treatments: (i) no N-P-K fertilizers or organics (NF), (ii) inorganic N-P-K fertilizer, (iii) N-P-K + pig manure (PM), (v) N-P-K + chicken manure (CM), (vi) N-P-K + rice straw (RS). The N-P-K fertilizers ($\text{N-P}_2\text{O}_5\text{-K}_2\text{O}$) were uniformly applied at a density of $270\text{-}135\text{-}180 \text{ kg/ha}^{-1}$ in the form of urea, single superphosphate, and a muriate of potash throughout the experiment. All fertilizer treatments had the same nitrogen and carbon content, while all manures were applied using the same carbon density of $2,850 \text{ kg}\cdot\text{ha}^{-1}$. The experiment management timetable is shown in Table 1.

2.3. Soil sampling, organic manure sampling and chemical analysis

Fresh soil samples (0–15 cm depth) in each field were collected using a stainless steel auger at various times during the rice growth period, corresponding to the seeding stage, tillering stage, jointing stage, heading stage, filling stage, milk-ripe stage and maturity stage. Six randomly extracted soil cores were mixed to produce a composite sample from each plot. After the removal of discrete plant residues and visible soil organisms, samples were analyzed or stored at 4°C , and used within 24 h for the estimation of EOC content via the method outlined in Graeme et al. (1995).

Soil samples were shaken (at 12 rpm) for 1 hour in 25 mL of 33, 167 and 333 mmol/L KMnO_4 . Oxidation of organic matter was measured in terms of the observed change in KMnO_4 concentration (33, 167 and 333 mmol/L), determined by spectrophotometer at 565 nm, with the results expressed as mg C g soil^{-1} (assuming 1 mmol/L MnO_4^- oxidises 9 mg C, Graeme et al., 1995). Fraction 1 was that part oxidised by 33 mmol/L KMnO_4 ; fraction 2 the 167 mmol/L KMnO_4 extraction minus the 33 mmol/L KMnO_4 extraction; and fraction 3 the 333 mmol/L KMnO_4 extraction minus the 167 mmol/L KMnO_4 extraction. In addition, the organic manure samples were passed through a 2.0 mm sieve and the EOC content measured as above.

2.4. Measurement of CH_4 flux

CH_4 flux was measured via the closed chamber method (Xionghui et al., 2012).

Table 1. Timetable of experiment management

Date	1-Jun	17-Jul	22-Jul	23-Jul	17-Jul to 1-Aug	2-Aug to 31-Aug	1-Sep to 25-Sep	25-Sep to 10-Oct	10-Oct
Event and paddy field status	Sowed	Applied organic manure	Applied chemical fertilizer	Transplant	Flooding	Drained	Intermittently re-flooded	Drained	Rice harvest

The chamber (55cm in diameter×120 cm in height) was placed on the water surface, sealing off the plot and rice plant, with 0.05 L gas samples manually taken from the chamber 0, 10, 20 and 30 min after placement, and the gas samples transferred into a 12 ml vacuum gas vial (Labco Exetainer® Labco Limited, UK). The CH₄ flux from each plot was measured once a week (9:00~10:00 a.m.) between June 21st and October 8th (a total of 17 times), calculated from the increase in concentration after 30 min and taking into consideration the average temperature in the chamber during this 30 min period.

The CH₄ concentrations of gas samples were analyzed in a packed-column gas chromatograph equipped with a flame ionization detector (GC-7890A, Agilent corp., American) and operated at 250°C. The injecting port temperature was 50°C and the carrier gas was high purity N₂ gas.

2.5. Statistical analysis

The mean flux over rice growth, EOC content in soil and organic manure was the average of all of the measured values during the study period. One-way ANOVA was applied in order to test for differences in EOC content and CH₄ flux among the five treatments, with a significance level of $p < 0.05$. Results are given as means and the difference between treatments were analyzed according to least significant difference (LSD) test at $p < 0.05$ with SPSS 17.0 (IBM, USA).

3. Results

3.1. Seasonal variation in CH₄ emissions under different fertilizers

CH₄ emission fluxes were high during the early growth stages, but fell gradually as the rice grew (Fig. 1). CH₄ emissions were still elevated during the period following the application of organic fertilizer in the jointing stage (September 5th), but was afterwards characterized by low levels which continued until rice maturity (Fig. 1).

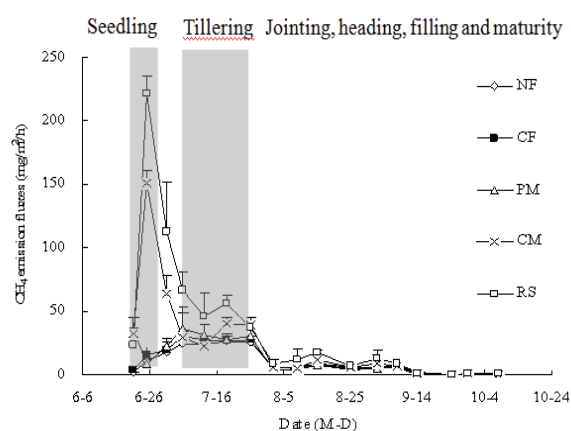
The CH₄ emission mode of treatment RS was similar to CM, while that of PM was the same as NF and CF (Fig. 1). RS methane flux peaked at 221.55 mg·m⁻²·h⁻¹, followed by CM at 128.20 mg·m⁻²·h⁻¹. In contrast, treatments PM, CF and NF all exhibited small fluctuations ranging from 1.49 mg·m⁻²·h⁻¹ to 30.40 mg·m⁻²·h⁻¹. Three flux peaks of CH₄ emission were observed among the different treatments:

whereas RS and CM peaked at the mid-seedling stage, tillering stage and heading stage, the other treatments peaked at the late seedling stage, tillering stage and heading stage. All treatments exhibited maximum emission during seedling and the tillering stage, which accounted for 60.67 %~81.1 % of total emissions during the entire rice growth period.

3.2. Variation in easily oxidizable organic carbon (EOC)

The EOC content of fraction 1 ranged from 1.73-3.60 g C kg⁻¹ dw⁻¹ (Fig. 2a). Levels increased to a peak on July 19th (tillering stage), before gradually decreasing until rice maturity, albeit with a slight increase on August 25th (filling stage). The minimum value observed throughout the entire rice growth period was recorded on October 8th (rice harvest). The EOC content of paddy soil under manure was higher than that under the other treatments, with RS and CM EOC levels obviously higher than those of PM, CF and NF. No significant differences in EOC content were observed between RS and CM, and between NF and CF.

The EOC content of fraction 2 (Fig. 2b) initially rose to a peak on July 19th (tillering stage) and afterwards decreased until a further increase was observed on September 24th (milk ripe stage). EOC levels then decreased until rice maturity. The EOC content of soil under RS was again higher than that under the other treatments; however, no significant differences between treatments were observed on July 1st (seedling stage).

**Fig. 1.** Seasonal variation in CH₄ emissions

The application of organic manure resulted in an obvious increase in EOC to levels higher than those under NF and CM on July 19th (tillering stage)

and August 2nd (jointing stage). On August 25th (heading stage), the EOC content of the RS and CM soils was higher than that under NF.

Fraction 3 EOC content exhibited large fluctuations during the rice growth period (Fig. 2c). Fraction 3 EOC content of RS soil was higher than that of CM, NF and CF. Although no significant difference between treatments was observed on July 1st (seedling stage), August 2nd (jointing stage), August 15th (heading stage) and October 8th (maturity stage), the fraction 3 EOC content of RS and CM was clearly greater than that of NF and CF on all other sampling occasions.

3.3. Variation in easily oxidizable organic carbon (EOC) in organic manure

The fraction 1 and 2 EOC content in organic manure followed the order RS>CM>PM (Table 2), and treatments differed significantly for fraction 1 EOC content. Fraction 2 EOC content in chicken manure was higher than that of rice straw and pig manure, where fraction 2>fraction 1>fraction 3 (in all treatments).

The EOC application density of fraction 1 in the three treatments followed the order RS>CM>PM, The EOC application density of fraction 2 in the three treatments followed the order PM>CM>RS, fraction 3 density was CM>RS>PM. Whereas the application density per hectare of fraction 2 was significantly different in all three treatments, that of

fraction 1 was significantly higher only in RS than CM and PM.

3.4. Relationship between soil EOC content and CH₄ emissions

A clear relationship was observed between fraction 1 and CH₄ emissions on July 1st (Table 3) and 19th, as well as on August 15th. In contrast, the EOC contents of fractions 2 and 3 correlated only significant with CH₄ emissions on July 19th. No correlation between EOC and CH₄ emissions was observed during the late growth period from August 25th until rice harvest.

3.5. Relationship between organic manure EOC content, application density and CH₄ emissions

Correlation analyses revealed most manure EOC content in manure and application density to be significantly correlated ($p<0.05$) with CH₄ emission fluxes for the different rice growth periods (Table 4). Fraction 1 EOC content in manure and application density tended to exhibit a positive correlation with emission fluxes, while fractions 2 and 3 in manure and application density were negatively correlated. The fraction 1 content and application density were significantly correlated ($p<0.01$) with accumulation emission fluxes. The fraction 1 content in manure and application density during the tillering stage (July 1 and 19) was significantly correlated with CH₄ emission.

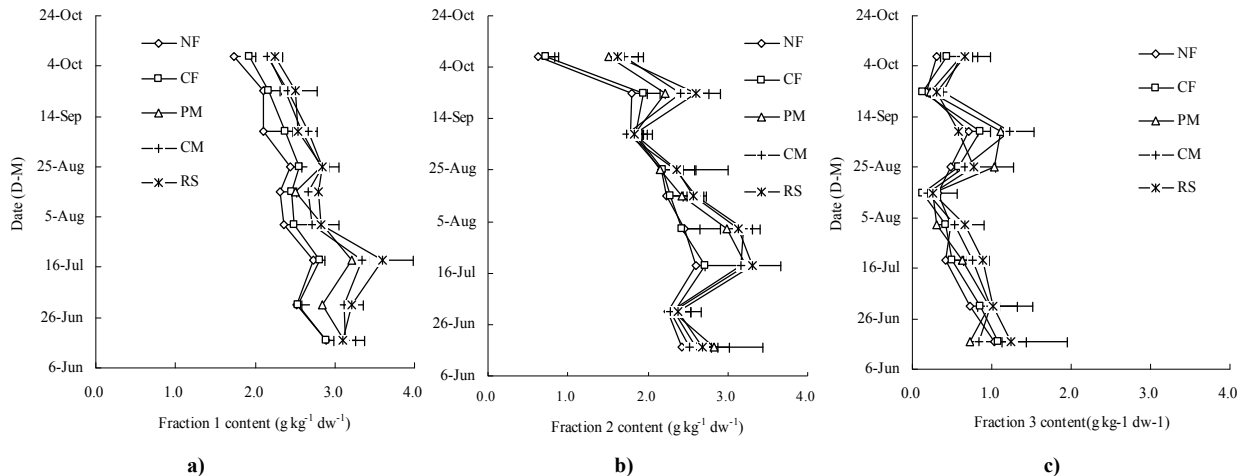


Fig. 2. EOC content of paddy soil during different rice growth stages: a) Fraction 1, b) Fraction 2, c) Fraction 3

Table 2. The EOC content of different fractions in organic manure

	Treatments	Fraction 1	Fraction 2	Fraction 3
Content of organic manure (g·kg ⁻¹)	PM	11.88 c	62.70 b	1.57 b
	CM	19.33 b	68.62 a	13.03 a
	RS	36.23 a	60.49 b	17.80 a
Application density per hectare (kg·ha ⁻¹)	PM	198.64 b	1048.17 a	26.31 b
	CM	206.73 b	733.85 b	139.39 a
	RS	270.32 a	451.33 c	132.79 a

Lowercase letters indicate significant differences between treatments at $p<0.05$ according to an LSD (least-significant difference) multiple-range test

Table 3. Pearson correlations for soil oxidizable organic carbon and CH₄ emission fluxes

	21-Jun	1-Jul	19-July	2-Aug	15-Aug	25-Aug	8-Sep	24-Sep	8-Oct
Fraction 1	0.488	0.675**	0.736**	-0.042	0.643**	0.207	-0.471	0.036	0.322
Fraction 2	0.347	0.059	0.536*	0.162	0.385	-0.112	-0.203	0.127	0.105
Fraction 3	-0.314	0.178	0.662**	0.249	0.106	-0.006	-0.696*	-0.014	0.352

** Correlation is significant at $P < 0.01$; *Correlation is significant at $P < 0.05$; $n=17$

Table 4. Pearson correlations for oxidizable organic carbon content and application density in manure and CH₄ emission fluxes

Type	Factions	21-Jun	1-Jul	19-Jul	2-Aug	15-Aug	25-Aug	24-Sep	8-Oct	Accumulation emission fluxes
EOC content in manure	Fraction 1	-0.437	0.914**	0.908**	0.608	0.857**	0.636	0.696*	0.548	0.901**
	Fraction 2	-0.043	-0.394	-0.419	-0.137	-0.606	-0.500	0.256	-0.150	-0.389
	Fraction 3	-0.377	0.699*	0.696*	0.531	0.652	0.573	0.811**	0.475	0.686*
EOC application density	Fraction 1	-0.279	0.827**	0.834**	0.520	0.817**	0.685*	0.505	0.595	0.829**
	Fraction 2	0.455	-0.861**	-0.852**	-0.630	-0.777**	-0.634	-0.818**	-0.550	-0.851
	Fraction 3	-0.094	0.354	0.294	0.451	0.271	0.501	0.388	0.283	0.344

** Correlation is significant at $P < 0.01$; *Correlation is significant at $P < 0.05$; $n=17$

4. Discussion

4.1. CH₄ emissions

A number of studies have demonstrated that methanogenesis and CH₄ production can be significantly increased by the presence of exogenous organic carbon (Chen et al., 2001; Yagi and Minami, 1990; Yang et al., 2010; Yuan et al., 2014; Wang et al., 2012), especially evident after the addition of rice straw. For example, Ma et al. (2009) found that CH₄ emission in a paddy field with straw application increased 3.9–10.5 times with respect to that without straw added. The present study also showed CH₄ accumulation emission to significantly increase after the application of manure. Compared with the chemical fertilizer treatment, CH₄ emissions increased by 1.15, 1.67 and 2.69 times in the PM, CM and RS treatments, respectively.

Many studies have identified a remarkable peak in methane flux during the rice growth period in Chinese paddy soils (Liu et al., 2008; Sheng et al., 2011). The largest CH₄ flux in soils under the NF, CF and PM treatments in the present study appeared during the tillering stage, followed by the seedling stage. This pattern is different to that associated with the application of chicken manure or straw, with maximum CH₄ flux observed during the seedling stage and the tillering stage second. This discrepancy may be due to the EOC content of soil fraction 1 under each treatment, for which the order was: RS>CM>PM.

Methane production was likely greater with the addition of straw because the EOC in fraction 1 is easily decomposed and utilized by microorganisms (Wang et al., 2011). Furthermore, not only were high CH₄ emissions observed in the paddy soil applied with pig manure, the paddy field itself also exhibited considerable methane flux without the addition of fertilizer during the tillering stage, when levels reached 119.7 kg/ha⁻¹. Therefore, the largest emission

of CH₄ from the soil under pig manure was observed during the tillering stage not only because of the manure, but also because of the paddy field itself.

4.2. Relationship between CH₄ flux and EOC content in manure and application density

The only method with which to increase soil organic carbon content is often the addition of exogenous organic carbon. As exogenous organic carbon differs in terms of the amount and type of soil organic carbon produced, the resulting carbon emissions also vary. Inevitably, some fractions of organic carbon are related to CH₄ emissions, with microbes decomposing organic matter into simpler forms representing the precursor to CH₄ formation (Ding and Cai, 2002).

Active organic carbon can be moved, decomposed and utilized by microbes as a carbon resource in the soil (Shen et al., 1999). A component of the active organic carbon pool, EOC is easily decomposed and changed in flooded paddy fields and our result showed that there is a close link between fraction 1 content in paddy soil and CH₄ emission. It maybe because that fraction 1 content was easily oxidizable in soil, prior to being utilized by microbes and the microbial community degrades EOC fraction 1 in to simpler compounds. Methanogens then use these simple simple compounds in the last step of the methanogenic fermentation. In the present study, a significant correlation was observed between soil fraction EOC content and CH₄ emissions during the tilling stage.

Furthermore, correlation analyses showed that the EOC content of fraction 1 of the applied manure correlated with both CH₄ flux during the tilling stage and CH₄ accumulation fluxes. The EOC fractions content and application density was a negatively related with the CH₄ emission, which warrant further study in to these specific carbon-microbe interactions.

Accumulated CH₄ fluxes and CH₄ fluxes were found to correlate with the EOC fraction I content of all manure fractions, during the tilling period. This result is in agreement with our anticipation that EOC associated with the application of organic manure can influence CH₄ emission fluxes.

It maybe that fraction 1 content was easily decomposition organic carbon in labile organic carbon by microbial. Our findings also demonstrate that the lower the fraction 1 EOC content, the lower the methane emission.

5. Conclusions

This study indicated that application organic manures was increased CH₄ emissions, the treatment of emission fluxes order was rice straw > chicken manure > pig manure > chemical fertilizer, soil organic carbon content showed the same order as methane emissions. The fraction 1 content in the soil organic carbon had a directly related with CH₄ emissions. Application low fraction 1 content organic manure maybe an effective methane to mitigating CH₄ emission.

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(Chisti, 1989), (Gavrilescu and Roman, 1996), (Moo-Young et al., 1999).

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Mauch K., Vaseghi S., Reuss M., (2000), *Quantitative Analysis of Metabolic and Signaling Pathways in Saccharomyces cerevisiae*, In: *Bioreaction Engineering*, Schügerl K., Bellgardt K.H. (Eds.), Springer, Berlin Heidelberg New York, 435-477.

Faber K., (2000), *Biotransformations in Organic Chemistry – A Textbook*, vol. VIII, 4th Edition, Springer, Berlin-Heidelberg-New York.

Handbook, (1951), *Handbook of Chemical Engineer*, vol. II, (in Romanian), Technical Press, Bucharest, Romania.

Symposia volumes: Names and initials of authors, year (between brackets), paper title, symposium name, volume number, place, date, page numbers:

Clark T.A., Steward D., (1991), *Wood and Environment*, Proc. 6th Int. Symp. on Wood and Pulping Chemistry, Melbourne, vol. 1, 493-498.

Journal papers: Names and initials of authors, year (between brackets), full title of the paper, full name of the journal (*italic*), volume number (**bold**), first and last page numbers:

Tanabe S., Iwata H., Tatsukawa R., (1994), Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals, *Science of the Total Environment*, **154**, 163-177.

Patents: Names and initials of authors, year (between brackets), patent title, country, patent number (*italic*):

Grant P., (1989), *Device for Elementary Analyses*. USA Patent, No. 123456.

Dissertations: Names and initials of authors, year (between brackets), title, specification (PhD Thesis, MSc Thesis), institution, place:

Aelenei N., (1982), *Thermodynamic study of polymer solutions*, PhD Thesis, Institute of Macromolecular Chemistry Petru Poni, Iasi, Romania.

Star K., (2008), *Environmental risk assessment generated by natural hazards*, MSc Thesis, Institute of Hazard Research, Town, Country.

Legal regulations and laws, organizations:

Abbreviated name, year (between brackets), full name of the referred text, document type, author, URL address:

ESC, (2007), Improving access to modern energy services for all fundamental challenge, Economic and Social Council, ENV/DEV/927, On line at: <http://www.un.org/News/Press/docs/2007/envdev927.doc.htm>.

EPA, (2007), Biomass Conversion: Emerging Technologies, Feedstocks, and Products, Sustainability Program, Office of Research and Development, EPA/600/R-07/144, U.S. Environmental Protection Agency, Washington, D.C., On line at: <http://www.epa.gov/Sustainability/pdfs/Biomass%20Conversion.pdf>.

EC Directive, (2000), Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000, on the incineration of waste, Annex V, *Official Journal of the European Communities*, L 332/91, 28.12.2000, Brussels.

GD, (2004), Governmental Decision No. 1076/2004 surnamed SEA Governmental Decision, regarding the procedure for strategic environmental impact assessment for plans or programs, *Romanian Official Monitor*, Part I, No. 707 from 5th of August, 2004.

Web references

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Citations of groups of references should be listed first alphabetically, then chronologically.

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