

PTIM 2015

1st International Caparica Conference on Pollutant Toxic Ions and Molecules

November 2nd – 4th 2015 | Caparica | Portugal

CONGRESS TOPICS

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Waste management | Catalytic elimination | Restoration and treatment of contaminated sites
Remediation and Bioremediation | Environmental contamination | Environmental control and
prevention | Emerging pollutants | Health effects | Medical treatments

Proceedings Book

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2nd – 4th November 2015

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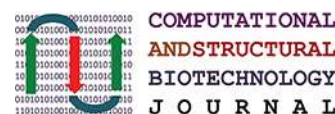
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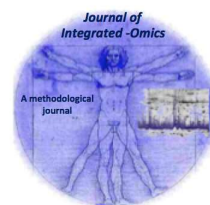
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Welcome

Dear Colleagues,

It is with proud that we welcome you to Caparica, one of the best-preserved maritime coasts from Iberian Peninsula. In addition to nurturing the scientific spirit among researchers from different areas, the 1st PTIM brings also the opportunity to enjoy the largest beach from Portugal.

The beach is away from the Village, and the venue is located on the natural park close to the coast.

There are tens of kilometres of white, fine sand to lie and relax in the sun. In addition, the capital of Portugal, the surprising always-ancient Lisbon is situated to 10 km. There are good ways of reaching the capital either by bus, car (taxi) or train.

If you have some free time, please find below a list of places you would like most likely to visit:

-Lisbon:

<http://www.golisbon.com/sight-seeing/top10.html>

-Sintra:

<http://wikitravel.org/en/Sintra>

We hope you will enjoy your stay with us.

Yours

The organizing committee

Preface

Pollutants, inorganic or organic, ionic or neutral, have the unmistakeable sign of men kind. They are the slow dead, which kills the life in our planet, kills our kids too, and kills us as well. Does life in Earth have a chance? This is a difficult question to answer. The pollution is so intense in some places of our planet that life has become compromise in them.

A recent study involving more than 30 000 women in the USA suggests that endocrine-disrupting pollutants, EDPs, are linked to earlier menopause. Just as another study done over 2 732 women suggesting that polyfluoroalkyl Chemicals has the same effects as EDPs. And what to say about the recent report alerting the raising mercury content in tuna at a level of 3.8% per year since 1998? Countless examples can be given.

The question still remains: are humans driving the planet till dead?

This question will be answered, or better to say, try to be answered during the 1st International Conference on Pollutant Toxic Ions and Molecules, PTIM2015 that will be held in November 2015 in Caparica, Portugal.

More than 152 participants from 48 countries will join the 1st PTIM 2015 conference. Delegations from Portugal, Spain, Italy, France, Poland, Romania, Japan, USA, China, Canada, Egypt, Bolivia, Belgium, Iran, South Arabia, Tunisia, Brazil, Ireland, Turkey, Algeria, Serbia, UK, Singapore, South Africa, Colombia, Mexico, Germany, India, Austria, Jordan, Malaysia, United Arab Emirates, Thailand, Czech Republic, Sweden, Philippines, Nigeria and Slovakia are confirmed.

On behalf of the organizing and scientific committees.

Truly Yours,

J. L Capelo, PhD.

Carlos Lodeiro, PhD.

Conference Chairs

PTIM

2nd- 4th November 2015, Caparica, Portugal

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Plenary Lectures

PL 1 - Sensing toxic metal ions by using “unselective” fluorescent chemosensors: concepts and applications

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Abstract

The design and synthesis of fluorescent molecular sensors that selectively respond to the presence of a given analyte (in particular a toxic metal ion) into a complex matrix is a vigorous research area of supramolecular chemistry. Applications can span from process control to environmental monitoring, food analysis, and medical diagnosis, to give some examples. From a structural point of view, the most common class of fluorescent chemosensors consists of a fluorogenic unit (signaling site) covalently linked, through an appropriate spacer, to a guest binding site (receptor unit). The selective host-guest interaction of the target species with the receptor unit (recognition event) is converted into an optical signal expressed as an enhancement or quenching of the fluorophore emission.

Very frequently, a fluorescent chemosensor based on this “receptor-spacer-fluorophore” supramolecular modular scheme is overall not thermodynamically selective for a given metal ion, but it can give a selective optical response in its presence. This is still a favorable case as compared to a chemosensor that shows both a thermodynamic and an optical response selectivity towards a given analyte.¹ The implications of this observation in terms of synthetic and mental approach to the development of fluorescent molecular sensors for metals and other type of analytes are significant. Rather than searching for a thermodynamic selective receptor for a given analyte to link to a fluorophore, the “complementary receptor-spacer-fluorophore” supramolecular synthetic approach of changing the coordinating signaling unit attached to a pre-defined receptor unit (not necessarily the best in the binding process) represents an easier alternative.² A “synergic” cooperation between the receptor and the signaling units can intervene in determining at least selectivity in the optical response of the chemosensor. Some significant examples of this approach to the development of fluorescent chemosensors for biologically and environmentally important metal ions will be given.^{3, 4}

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PL 2 – Integrated Metallomics and Metabolomics in Metal Pollution Assessment

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Abstract

Anthropogenic and natural activities have increased the contaminants levels in terrestrial and aquatic ecosystems. In this sense, the importance of monitoring the exposure and studying the effects of heavy metals on living organisms has increased in the last years. Studies of small mammals for evaluate terrestrial ecosystems, mainly free-living mice (*Mus spretus*), and crayfishes (*Procambarus Clarkii*) for aquatic ecosystems have been used as bioindicators in numerous environmental studies because they can provide useful information for assessment of risk of metals to humans¹⁻³. In the present work, we consider the use of mice and crayfishes to assess its biological response or mode of actions against metal contaminants. The results have been applied in the relevant ecological area of Doñana National Park and surroundings (southwest Spain). In order to obtain a global vision about metal toxicity mechanisms and the responses that metals elicit in the organisms, new and more potent methodologies are needed.

Omics technologies (genomics, transcriptomics, proteomics/metallomics, metabolomics and ionomics) offer a valuable alternative in this field since they provide massive information about biomolecules in cells and organisms under toxic metals effects. *Omics* differs from traditional hypothesis-driven research because it is a discovery-driven approach and they provide a more general appraisal of molecules altered under pollutant exposure. We demonstrated here the successful applications of heterologous microarrays, proteomics methodologies (2-DE, iTRAQ®), metallomics, ionomics or metabolomics in separated studies. Nevertheless, an overall evaluation of changes that contaminants induce in cells is only possible by the integration of *-omics*, since the transcripts induced by pollutants (transcriptomics) encode proteins with altered expression profiles, which undergo post-transductional modifications (proteomics). In addition, many proteins related to environmental issues are bound to metals that make advisable the use of metal-tagged techniques (metallomics) and most of them are related to oxidative stress enzymes. Moreover, metabolomics and ionomics provide information about what is actually happening in the organisms, since metabolomic and ionic

profiles also reflect the influence of external factors (metal exposure, diet), providing easier understanding of complex biological systems under environmental issues.

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Key Words: metabolomics, metallomics, ionomics, transcriptomics, environment, living-organisms

Acknowledgements: This work was supported by the projects CTM2012-38720-C03-01 from the Spanish Ministry of Economy and Competitiveness and P12-FQM-0442 from the Regional Ministry of Economy, Innovation, Science and Employment (Andalusian Government, Spain).

PL 3 – Genomic/proteomic changes in rat brain after acute and chronic exposures to particulate matter in Los Angeles basin air: Comparison with human brain tumors

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Abstract

Air pollution negatively impacts pulmonary, cardiovascular, and central nervous systems. Although its influence on brain cancer is unclear, toxic pollutants can cause blood-brain barrier disruption, enabling them to reach the brain and cause alterations leading to tumor development.

Methods: A. By gene microarray analysis validated by quantitative RT-PCR and immunostaining we examined whether rat (n=104) inhalation exposure to air pollution particulate matter (PM) resulted in brain molecular changes similar to those associated with human brain tumors. Global brain gene expression was analyzed after exposure to PM (coarse, 2.5-10 μm ; fine, < 2.5 μm ; or ultrafine, < 0.15 μm) and purified air for different times, short (0.5, 1, and 3 months) and chronic (10 months), for five hours per day, four days per week. Expression of select gene products was also studied in human brain tumors (n=83).

B. Heavy metal analysis from brain tissue was conducted by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) as follows: half of the brain (0.5 g) was homogenized and submitted to heavy metal analysis (GLP certified laboratory Exova, Santa Fe, CA) using the ICP-AES method and the other half of the brain was used for gene array analysis. Briefly, a weighed aliquot of brain was treated for 1 hour at 110°C with a mixture of 0.5 mL nitric acid (36% w/v) and 0.5 mL hydrochloric acid (86% w/v). After cooling, 0.5 mL hydrogen peroxide (30% w/v) was added and incubated for another 30 minutes. Measured values were expressed in means \pm SD. Differences between experimental groups were analyzed by the Wilcoxon-Mann Whitney Test assuming $p < 0.05$ as significant.

Results: *Arc* and *Rac1* genes, and their protein products were selected for further examination. *Arc* was elevated upon two-week exposure to coarse PM and declined after 10-month exposure. *Rac1* was significantly elevated upon 10-month coarse PM exposure. On human brain tumor sections, *Arc* was expressed in benign meningiomas and low-grade gliomas but was much lower in high-grade tumors. Conversely, *Rac1* was elevated in high-grade vs. low-grade gliomas. *Arc* is thus associated with early brain changes and low-grade tumors, whereas *Rac1* is associated with long-term PM exposure and highly aggressive tumors.

Rats have a lifetime of about 2 years, and this heavy metal accumulation was observed in young rats of 2 to 5 months of age, which translates to an age < 18 years in human. Thus, we can conclude that significant heavy metals accumulation was detected in the animal brain tissues in short period of exposure, up to three months, by 30% (Co), 400% (Ni), 75% (As), and 75% (Zn). Studying the accumulation of heavy metals in the rat's brain we have observed increased gene expression levels of pro-inflammatory genes within 3 months of exposure to fine and ultrafine particles, which also corresponds to the heavy metal accumulation in brain of the exposed rats. This study found a correlation between the presence of heavy metals and turning on of a set of genes, which have been indicated to be responsible for neurodegenerative diseases. These data clearly show the effect of air pollutants on the brain pathology and urgent need to curb the pollutants emission.

In summary, exposure to air PM leads to distinct changes in rodent brain gene expression similar to those observed in human brain tumors.

Key words: air pollution particles, chronic exposure, gene microarray, brain tumor, Arc, Rac1

PL 4 – Capture and Conversion of Micropollutants from Drinking Water Supplies: Engineered Solutions

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Abstract

Purpose: To develop, model, optimize, and experimentally validate a novel integrated concept based on the use of appropriate ion-exchange membranes with dedicated properties, which can act as barriers between a contaminated drinking water stream, containing one or more target ionic micropollutants, and a biological (or chemical) compartment, in which a microbial culture able to degrade (transform) these micropollutants to harmless products (or appropriate chemical coagulants, when a biological conversion is not feasible) are present.

Experimental description: A number of different membrane module configurations within broad ranges of the process controlling operation parameters, such as pH, temperature, redox-potential, ionic composition and concentration, fluid hydrodynamic conditions have been investigated. Various analytical methods, such as HPLC (*e.g.*, Dionex, USA and Biorad, USA), AAS (Thermo, UK) ICP-AES (Horiba Jobin-Yvon, France), Fluorescence *in situ* hybridization (FISH) analyzed via epifluorescence microscopy (Olympus, Japan), Confocal laser scanning microscopy (Zeis, Meta, Germany), Gas-sensitive electrode measurements (Thermo, USA), total organic carbon (TOC) measurements (Shimadzu Hapan), etc. as well as a number of advanced mathematical and simulation tools for multivariate statistical data analysis and computational fluid dynamics (CFD) have been applied.

Results: A number of experimental, modeling and process validation / scale-up related results on the removal of various drinking water micropollutants, such as nitrate, nitrite, perchlorate, bromate, arsenate and ionic mercury, for which the proposed maximum allowed guideline concentration values for acceptable drinking water quality are within the ppb to ppm range, due to their carcinogenic effects or other risk factors to public health, have been obtained. Since some of these micropollutants may also be present simultaneously in a contaminated drinking water, the possibility of their simultaneous removal through the novel concept proposed was explored and proved feasible for implementation. For example, bromate, perchlorate and nitrate when simultaneously present in a contaminated water were simultaneously transported through the membrane to a biocompartment, where a mixed microbial culture was able to biodegrade nitrate, perchlorate and bromate efficiently to nitrogen, chloride and bromide, respectively, as electron acceptors. The concentrations of these three target anions, in the treated water stream, were all reduced well below their recommended maximum contaminant levels in drinking water.

Conclusions: The results obtained through this systematic research are highly promising since they demonstrate that target trace pollutants could be efficiently removed from both low and high salinity multi-ionic water streams, which opens new and exciting horizons for future possible applications of the proposed novel integrated concept.

Key Words: Micropollutants, Drinking water, Removal, Ion-exchange membranes, (Bio)chemical conversion

Acknowledgements: A number of our MSc and PhD students as well as other grant holders have been involved in the technical / experimental and/or analytical work related to the development and validation of this concept. Therefore the authors gratefully acknowledge their tireless dedication and great enthusiasm.

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PL 5 – Recent developments in automatic bioaccessibility tests of trace elements in environmental solids based on flow analysis

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Abstract

In this presentation, dynamic column-based extraction and fractionation is presented as a new methodological approach for risk assessment and exposure of potentially hazardous trace elements in environmental solids [1]. Different platforms for automatic assays capitalized on the various generations of flow analysis are overviewed and critically assessed. Pros and cons for ascertainment of bioaccessible metal forms under conservative conditions within the framework of environmental availability are also pinpointed.

Limitations of flow-based microcolumn fractionation methods based on peristaltic pumps as liquid drivers [2] in terms of undue flow backpressure, lack of sample representativeness and impaired sample throughput have been overcome in our research group by the exploitation of liquid drivers enduring moderate pressure drops, the design of appropriate sample containers and multiple-extraction automatic devices along with the extraction of samples under fluidized-bed conditions [1,3,4]. In addition, automatic processing of leachates by sorptive microextraction techniques involving on-chip mesofluidic platforms [5] and dispersed carbon nanomaterials [6] fostered the reliable quantification of the most ecotoxicologically significant forms of hazardous elements in solid substrates at the sub-ng/L level.

The lecture also summarizes novel applications of dynamic extraction/fractionation as a valuable tool for investigation of the potential reuse of solid wastes (e.g., bottom ash) for civil engineering works [4,7], for inferring whether or not biomass (biofuel) resources might be fired in combustion devices [8,9], and also for elucidation of the efficiency of biochar amendments in soil remediation [10] as compared with phytotoxicity assays.

Recent results in our lab using permselective microdialysis membranes of appropriate molecular-weight cut off (ca. 30 kDa) to mimic the diffusive transport of metal species through the human epithelium of the small intestine are also presented for *in-vitro* investigation of metal bioavailability from contaminated soils (taken accidentally by children in playgrounds) or foodstuff using the validated UBM (Unified Bioaccessibility Method) by the BARGE consortium using gastrointestinal fluid surrogates [11].

The potential of advanced flow analysis methodology for automation of batchwise methods [12] and dynamic bioaccessibility tests [13,14] as a front end to atomic absorption/emission spectrometry or miniaturized

detection systems for real-time monitoring of the kinetics of metal extraction in soil environments and detection of steady-state or worst-case scenarios is also discussed in details.

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KeyNotes

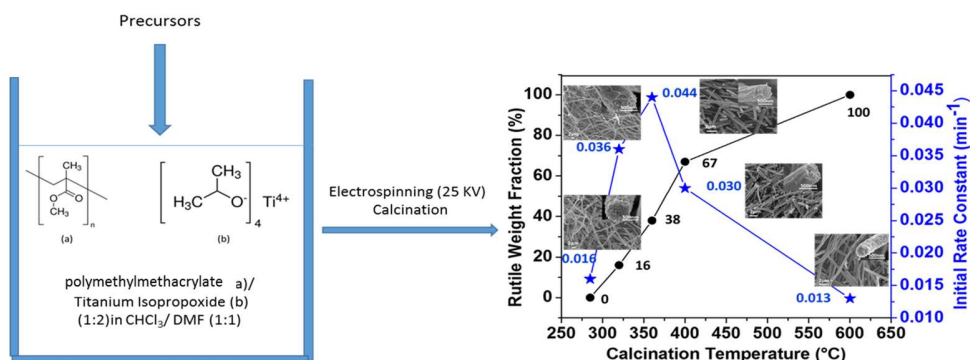
K 1 – Inorganic/organic hybrid nanomaterials and photocatalysis for removing industrial and environmental toxins from the environment

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Abstract

Toxins represent a challenge to the environment and in many cases human health. From industrial waste to biopharmaceuticals and synthetic agents, there is a need for new remediation methods to protect society. Combinations of organic and inorganic nanostructures have been created as catalysts to assist in this effort. Nanoparticles and nanofibrous semiconductors such as TiO_2 can be prepared which drive photochemical processes leading to oxidation, reduction, and radical initiated degradation.



New photocatalytic materials have been developed which can be applied to solve these environmental problems. The synthesis, design, and molecular characterization of recent electrospun nanomaterials and composites will be discussed. Insight into the critical role of grain size, electron injection, and hole injection will also be discussed in order to provide new insights into the design of future degradation systems.

Key Words: Nanofibers, Photocatalysis, TiO_2 , Biopharmaceutical degradation

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K 2 – Organic Micro-Pollutants in Environmental Systems: Analysis and Occurrence

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Abstract

In general, we can consider as micro-pollutants those contaminants present in the environment in concentration levels of $\mu\text{g.L}^{-1}$ or lower. Among these contaminants we may include emerging contaminants and antifouling compounds. The emerging contaminants are not currently covered by existing regulations. However, the possibility of adverse effects on humans and animals and their extensive environmental distribution have recently attracted increasing interest. In particular, these compounds include pharmaceuticals, surfactants, personal care products and hormones among others. On another hand, antifouling compounds are compounds introduced by manufacturers in the ship and yacht paints to avoid the biofouling accumulation and their presence in the environment can produce toxic effects in the natural ecosystems.

In this lecture we present several study cases of the analysis and presence of different contaminants belonging to the compound families aforementioned. Analytical procedures, determination techniques and occurrence in different environmental samples will be described with special attention to liquid chromatography with mass spectrometry detection technique and environmental samples like wastewater, sludge, seawater and marine sediments.

Keywords: emerging contaminants, antifouling, liquid chromatography, mass spectrometry detection

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K 3 – Water Purification Using Magnetic Nano- and Microparticles: Removal Effectiveness, Particles Reuse and Pollutant Recovery

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Abstract

Nanoparticles are attractive to many researchers because they are effective for metal and organic removal due to their high surface area to volume ratio and greater number of reactive sites. Magnetic nanoparticles (MNPs) are the advanced development of nanoparticles because of its added-value of magnetic property, which enhances their wide-ranging applications of environmental remediation. Sol-gel and co-precipitation methods are the two common methods for synthesizing iron-based MNPs (such as γ -Fe₂O₃, MnFe₂O₄, metal-doped γ -Fe₂O₃ etc.). The preparation of iron-based MNPs is safe, simple, and inexpensive. The magnetic nanoparticles can be characterized using X-ray diffractometer (XRD) for crystal identification, transmission electron microscopy (TEM) for size and morphology investigation, BET analyzer for surface area measurement, and vibrating sample magnetometer (VSM) for magnetic property and behavior analysis.

The application of MNPs for the removal of heavy metals from electroplating industrial wastewater has also been demonstrated. After wastewater treatment, the recovery of MNPs by the magnetic separation technique makes its potential to achieve complex environmental separations. Apparently, the magnetic nanoparticles possess the advantages of large surface area, high number of surface active sites, and high magnetic properties, which lead to high adsorption efficiency, high removal rate of contaminants, and easy and rapid separation of adsorbent from solution via magnetic field. However, on the subject of the recovery and regeneration of spent nanoparticles, little field information is available because of their difficulties of applying magnetic field in a real application. The efficiency of magnetic separation is influenced by the size of nanoparticles and the magnetic force, and thus a trade-off between the particle size and the applied magnetic force should be of consideration with respect to their technical feasibility. In this paper, the focus would be on the environmental application of MNPs, their effectiveness and removal mechanisms, the challenges being faced for industrial applications, potential solutions for solving the technical problems as well as future development of the MNPs.

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K 4 – Binding and optical sensing of inorganic polluting anions

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Abstract

There is a growing interest for molecular receptors able to bind, sequester and signal toxic and/or polluting anionic species.^{1,2} In fact, polluting anion can be either naturally present or spread in the environment by human activities. Beside the well known case of phosphate anions, whose large use in intensive agriculture leads to fresh and marine water eutrophication, other examples can be fluoride, often naturally occurring in ground water in high and toxic levels, arsenic derivatives, released by volcanic and geothermic activities and selenium anionic species, whose presence in the environment is due to its increasing use in photovoltaic devices. In consequence, the development of molecular tools able to strongly bind, sequester and/or optically detect these specie represents a current challenge in environmental chemistry.

In this context, two main approaches have been be exploited to bind polluting anions, based on the use of polyammonium cations or complexes with transition metals as receptors for anionic species. While the former can recognize anionic species basically via charge-charge interactions and hydrogen bonding, in the latter the metal ion is used as anchoring point for the guest anion. The addition of a fluorogenic units within the receptor structure may lead to fluorescent hosts suitable not only for binding but also for signaling of anions. To this purpose we are involved in the study of polyamine ligands, in most cases macrocyclic or macropolycyclic ligands containing fluorescent moieties, as anion binders in water.^{2,3} In fact, they can form polyammonium cations even at neutral pH and stable Zn(II) complexes, often featuring fluorescent emission and therefore suitable for quantitative signaling of anionic species. This study, carried out by coupling potentiometric, UV-vis and fluorescent emission measurements in aqueous solution has shown that selective binding and optical sensing of anions, such as polyphosphates, fluoride and seleniate can be achieved by an opportune tuning of the receptor characteristics. The molecular recognition event, in fact, results strongly dependent on the dimension and shape of the macrocyclic cavity as well as on the positive charge gathered on the ligand framework. In the case of Zn(II) complexes, the binding/signaling properties are also influenced by the number of coordinated metal ions and by their coordination environment.

Key Words: molecular recognition, anion binding, fluorescence signalling

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K 5 – Are fish a reliable biological model for nanotoxicology studies? Clues from previous studies

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Abstract

Over recent years, world has witnessed a dramatic increase of nanotechnology. Novel nanomaterials have been developed with surprising characteristics and applications in diverse industrial processes. In this sense, nanotechnology has attracted great attention for new developments in diverse areas such as biomedicine, chemistry or environment among others. However, their unique properties (small size, shape and surface area), that makes them distinctive are the same that can potentiate risks for living organisms. In fact, today massive amounts of nanomaterials are used in industry with consequent release of large quantities that ultimately reach aquatic environments. Therefore, it is mandatory to develop nanotoxicity studies to assure safety not only to ecosystems but also to Human health.

Thus, nanotoxicology increased in importance near the public and scientific community which resulted in several studies with the aim of providing information on this issue. Studies have been using diverse biological models: single cells, small invertebrates and vertebrates. Fish have been used as vertebrate model for investigating the effects of nanomaterials at the organism level, but also for studying the accumulation of these materials in tissues, or measuring sub-lethal parameters (e.g. biochemical reactions such as oxidative stress, gene expression, lipid peroxidation, etc.). Consequently, nanotoxicity mechanisms and effects can be assessed at different length scales (genes, cells, organisms). However, often the results seem contradictory or non-correlated. Some reasons for this are based on studies with different designs or diverse exposure periods which make them difficult to compare while other are related to distinct mechanisms of response provided by cells or whole organisms.

A series of nanotoxicity studies were developed by our group using distinct fish species (*Carassius auratus* and *Danio rerio*) and cells (HEPG2 MCF-7 human breast cancer cells) exposed to several types of nanoparticles (e.g. TiO₂, ZnO).

In this context, here we discuss fish as reliable biological models for *in vivo* nanotoxicology studies by comparing with results from *in vitro* assays using cells and studies using other animals.

Key Words: nanotoxicology, nanoparticles, fish, cells

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K 6 – Oral bioaccessibility of metals in simulated gastro-intestinal and lung fluids

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Abstract

Children are particularly sensitive to contaminant exposure. They are regularly exposed to toxic substances such as metals and metalloids via multiple pathways, including incidental soil ingestion and inhalation of particulate matter (PM). Finer fractions of soil and airborne PM may contain higher levels of metals, and therefore can contribute to carcinogenic risk via inhalation of suspended particles in air. Moreover, object mouthing is a common behavior for children and mouthing frequency and duration are especially high for infants and toddlers (1-3 y). In addition to inhalation and ingestion pathways, research has shown that metallic toys and low-cost jewelry mouthing and ingestion are also significant sources of exposure to potentially toxic elements. The socio-economical costs and adverse health effects of children's exposure to environmental contaminants are well documented. In addition to cognitive deficits related to blood Pb levels, exposure to As, Mn, and Cd has also been associated with neurodevelopment and behavioral disorders in children. Mouthing and ingestion of contaminated soil or children's consumer products and inhalation of coarse (PM₁₀) and fine particles (PM_{2.5}) may cause the release of contaminants via contact with saliva, gastro-intestinal or lung fluids depending on the exposure pathway. This may result in contaminant release into the systemic circulation.

Oral bioavailability is the fraction of a contaminant reaching the systemic circulation from the gastro-intestinal tract after ingestion, and oral bioaccessibility is the fraction of the substance that becomes soluble in the gastro-intestinal tract and is thus available for absorption. It must be noted that the coarser inhaled particles are ingested (gastro-intestinal pathway) but that an important fraction of inhaled fine particles (PM_{2.5}) is expected to be deposited in different lung regions, and therefore could significantly contribute to carcinogenic risk.

Bioaccessibility can be used as an estimation of bioavailability and, when available, in-vitro bioaccessibility tests might be preferred over in-vivo bioavailability tests for their cost advantage and ethical considerations. Incorporating contaminant bioavailability in terms of bioaccessibility and using bioaccessible concentrations instead of total concentrations in human health risk assessment studies should provide more accurate results.

This paper will present an overview of our work on the development and application of improved in-vitro assays for oral bioaccessibility assessment (ingestion and inhalation) of metals in contaminated soils, airborne particulate matter and children's consumer products. The paper will also highlight the research needs to refine

human health risk assessment using the bioaccessibility concept, therefore allowing for better protection of children's health.

Key Words: Heavy metals; Metalloids; Gastro-intestinal bioaccessibility; Lung bioaccessibility; Human health risk assessment; Consumer products; Suspended particulate matter; Contaminated soils.

Acknowledgements: The author acknowledges the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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K 7 – Chemical sensors based on porphyrins for detecting pollutant toxic ions

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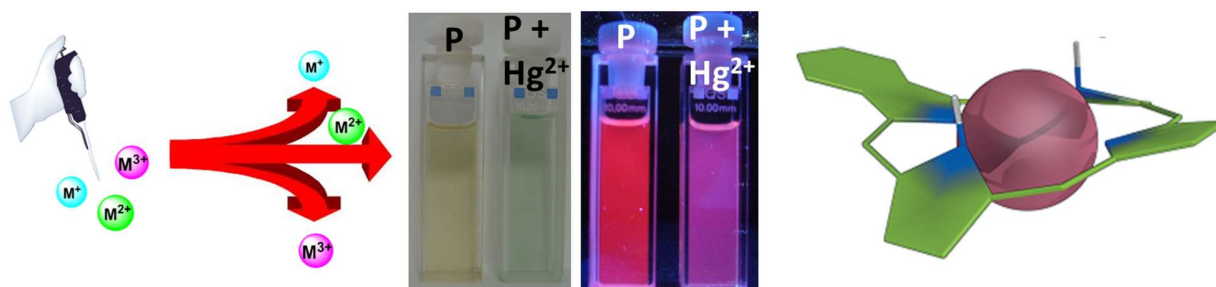
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Abstract

Purpose: The chemical and physical properties displayed by tetrapyrrolic macrocycles render them particularly attractive to be used in a wide range of fields like supramolecular chemistry, catalysis, electronic materials, sensors and medicine. The development of new colorimetric/fluorescent sensors for metal ion recognition is an area in high expansion due the advantages in terms of sensitivity, selectivity, response time in contrast with others analytical techniques usually used for metal ion detection. The selective detection and monitorization of metal ions using simple techniques based on optical detection are of particular interest due to their high toxicity for living organisms or their significant roles in biological, environmental and industrial fields. In particular, porphyrins and analogues are considered attractive candidates to be used as fluorescent and colorimetric chemosensors due to their remarkable photophysical properties.

Results: The sensing ability of different series of porphyrinic derivatives was studied in solution, gas phase, and on solid-supported polymers towards different metal ions. Significant changes in the ground and excited state were observed for metals such as Cu(II), Zn(II), Cd(II) and Hg(II). Some of them presented a significant and unexpected increase in the emission intensity in the presence of Hg(II). The studied compounds are also able to detect metal ions in gas phase and when immobilized in solid-supports.



Conclusions: We were able to prepare from readily available *meso*-tetraarylporphyrins *beta* substituted derivatives with different moieties through simple and efficient synthetic approaches that demonstrated sensing ability towards metal ions in solution, gas-phase and when supported in solid polymers. These new emissive hybrid inorganic–organic materials have the potential to be also explored as metal-ion chemosensors.

Keywords: Porphyrins, Metal ions, Binding Studies

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Oral Presentations

O 1A – Fly-ash based composites in simultaneous adsorption and photodegradation for up-scalable advanced wastewater treatment

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Abstract

Purpose: In most cases, various contaminants, with different chemical composition are simultaneously released into the environment. A typical example is the dye finishing industry, where residual dyes, heavy metals, surfactants are the main pollutants in wastewaters. The use of fly ash (FA) in wastewater treatment, for heavy metals and dyes immobilizations, represents a good application for solving the problems of advanced treatment and the intelligent use of this waste. For advanced removal of heavy metals and dyes we propose two concurrent, simultaneous processes, of adsorption and photocatalysis based on a composite of catalysts and fly ash. This paper presents the results when using a composite of TiO₂ and FA (FUSD4), in a one step treatment process of wastewaters containing heavy metals and dyes.

Experimental description: The 20–40 µm fractions were selected after sieving, and used to obtain a novel composite by mixing with the TiO₂ photocatalyst (Degussa P25, ca.80% anatase, and 20% rutile). The new composite (FUSD4) was obtained in an autoclave from the slurry of the powder mixture (fly ash, TiO₂ and NaOH) under stirring. After filtration, washing and drying at 105–120°C till constant mass, the dried FUSD4 substrate was obtained and further used in photocatalytic and adsorption experiments. XRD, SEM and EDX were used to evaluate the crystallinity, composition, and surface morphology. Surface characterization was completed by microporosity analysis (AFM) and BET surface measurements. The adsorption, the UV and VIS-photocatalytic properties of the composites were evaluated in pollutants systems containing methylene blue (MB) and a heavy metal (Cd²⁺). Experiments aimed at optimizing the pollutant concentration, the process duration, the mass of substrate, the process pH and were performed under stirring, under UV simulated solar radiation.

Results: The use of this composite must consider also the effect of the heavy metals on TiO₂ activity, along with the parallel process involving the dyes and the fly ash. Before investigating this double process, studies on the adsorption of the individual components must be performed on substrate mixtures. We report here the cadmium and methylene blue adsorption on mixtures of TiO₂ and fly ash collected from CET Brasov Romania. The process efficiency and kinetic is reported and correlated with the substrates characteristics. According to the results, this composite operates similarly to TiO₂, due to the similar values of the band gap energy and the band edge wavelength.

Conclusions: The efficiency data show - if optimized fly ash can be a suitable substrate for efficient adsorption and photodegradation of a complex pollutants from wastewaters. The development of composites materials, starting from fly ash obtained in very mild conditions by hydrothermal synthesis with low cost - efficient materials for up-scalable processes.

Key Words: fly ash, composite, simultaneous processes

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O 2A - Important factors affecting biodegradation of 17- α ethinylestradiol in wastewater treatment

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Abstract

Purpose: Municipal wastewater treatment plant (WWTP) effluents are a major contributor of estrogen endocrine disrupting compounds (EDCs) in the aquatic environment. The synthetic estrogen, 17 α -ethinylestradiol (EE2) has an EDC potency that may be over 10-times greater than the natural estrogens. EE2 is biodegraded in activated sludge processes by heterotrophic bacteria but the specific bacteria degrading EE2 in such a mixed culture has not been defined. Because different activated sludge process conditions may select for different bacteria our aim was to determine if process conditions that are known to provide selective pressures for different heterotrophic organisms affect estrogen biodegradation kinetics.

Experimental description: Lab-scale activated sludge sequencing batch reactors (SBRs) were operated at 20°C to study the impacts of metabolic and kinetic selection on EE2 degradation kinetics. The SBRs were fed primary effluent from a local WWTP supplemented with acetic acid. All reactors were operated for three solid retention times (SRTs) prior to measuring estrogen biodegradation kinetics under metabolic and kinetic selector conditions. The effect of metabolic selection on estrogen biodegradation kinetics was studied by SBR operation with aerobic-only, anoxic/aerobic, and anaerobic/aerobic process phases after feeding. The effect of kinetic selection studied by SBR aerobic operations at the same solids retention time (SRT) but with feeding at a high food/mass (F/M- gCOD/gVSS-d) ratio, a low-F/M ratio, and at a high-F/M ratio but with a smaller portion of readily biodegradable chemical oxygen demand (rbCOD). The influent wastewater was supplemented with 250 ng/L of E1, E2, and EE2. Estrogen measurements were taken in duplicate and measured by LC-MS/MS. EE2 biodegradation was assumed to follow a pseudo first-order model: $\frac{dE_{tot}}{dt} = -k_b X_{VSS} E_{sol}$ and $dE_{tot}/dt = k_b X_{VSS} E_{sol}$ where E_{tot} is the total EE2 concentration (ng/L), E_{sol} is the soluble EE2 concentration (ng/L), X_{VSS} is related to the biomass concentration (g VSS/L), and k_b is the pseudo first-order EE2 biodegradation coefficient (L/g VSS-d).

Results: EE2 biodegradation kinetics was normalized to mixed liquor volatile suspended solids (VSS). First order kinetic rate coefficient (k_b) values ranged from 5.0 to 18.9 L/g VSS/d at temperatures of 18 °C to 24 °C. EE2 k_b values for aerobic biomass growth at low initial F/M ratio feeding conditions (F/M_f) were 1.4 to 2.2 times greater than that from growth at high initial F/ M_f. Anoxic/aerobic and anaerobic/aerobic metabolic bioselector reactors achieving biological nutrient removal had similar EE2 k_b values, which were lower than that in aerobic reactors with biomass growth at low initial F/M_f. These results provide evidence that population

selection with growth at low organic substrate concentrations can lead to improved EE2 biodegradation kinetics in AS treatment. When the feed biodegradable COD:EE2 ratio was higher a lower effluent estrogen concentration was found.

Conclusions: Population selection conditions affect EE2 biodegradation kinetics. EE2 biodegradation in activated sludge processes is more efficient for system that select for slower growing bacteria and a lower effluent EE2 concentration is possible for systems with higher feed biodegradable COD:EE2 ratios.

Key Words: 17 α -ethinylestradiol, EE2, activated sludge, bioselector, biokinetics

Acknowledgements: This research was supported by the U.S. National Science Foundation and the Seattle, Washington King County Wastewater Treatment Division Graduate Student Research Fellowship program.

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O 3A - Stimulating antibiotic removal from wastewater through bioaugmentation

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Abstract

Purpose: A strain identified as *Achromobacter denitrificans* found to be capable of sulfamethoxazole (SMX) degradation was studied for bioaugmentation in wastewater treatment plants (WWTP). This study investigated the kinetics of SMX degradation by *A. denitrificans* at different concentration ranges, to assess the feasibility of using it for bioaugmentation.

Experimental description: The SMX degradation tests by *A. denitrificans* were carried out in a 10 L bioreactor where SMX was fed at 20 µg/L or 600 ng/L of SMX, at 30°C, 200 rpm stirring, and aeration of 1 vvm (gas volume flow/unit of liquid volume/minute). In some tests, the bioreactor contained an additional 10mM of acetate or succinate as supplemental C-source, while an adsorption control test was performed through addition of NaN₃ (2g/L) to inhibit bacterial activity. Solid Phase Extraction (SPE) was performed as a pre-concentration technique prior to SMX quantitative determination by Liquid Chromatography – tandem Mass Spectrometry (LC-MS/MS).

Results:

Table 1. Reaction rate coefficient (k_{bio}) for SMX degradation by *A. denitrificans*

Augmented seed	Matrix	SMX concentration	k_{bio} (L.gX _{ss} ⁻¹ .d ⁻¹)	Reference
Activated sludge	Preclarified wastewater	Hundreds ng/L	0.41	(Plosz et al., 2010)
<i>A. denitrificans</i>	Media w/o other C-source	600 ng/L	0.84	This study
<i>A. denitrificans</i>	Media w/o other C-source	20 µg/L	32	This study
<i>A. denitrificans</i>	Media with acetate	600 ng/L	17.7	This study
<i>A. denitrificans</i>	Media with acetate	20 µg/L	808	This study
<i>A. denitrificans</i>	Media with succinate	600 ng/L	10.2	This study

It is clear from Table 1 that the first-order reaction rate coefficients (k_{bio}) increased in the presence of an additional easily biodegradable substrate. Our results demonstrated that the kinetics of SMX degradation by *A. denitrificans* compares favorably with activated sludge. For the level of µg.L⁻¹ of SMX, the k_{bio} of the culture was

2 to 3 orders of magnitude higher, i.e. 32 and 808 $\text{L.gX}_{\text{ss}}^{-1}.\text{d}^{-1}$ for tests fed without and with a supplemental carbon source (acetate), respectively, than that of non-augmented activated sludge of 0.41 $\text{L.gX}_{\text{ss}}^{-1}.\text{d}^{-1}$ (Plósz et al., 2010). In the level of ng.L^{-1} , the strain only exhibited substantially higher reaction rate coefficients (k_{bio}), i.e. 17.70 or 10.20 $\text{L.gX}_{\text{ss}}^{-1}.\text{d}^{-1}$, for tests fed with acetate or succinate as a supplemental carbon source, when compared to that of non-augmented activated sludge. The simultaneous consumption of acetate and SMX (results not shown) suggested that a co-metabolic mechanism was important in increasing the SMX degradation rate. During the degradation of SMX by *A. denitrificans*, the accumulation of 3-amino-5-methylisoxazole was observed as the only metabolite (data not shown).

Conclusions: *A. denitrificans* is capable of SMX degradation in the presence or absence of C-source at low levels of SMX ($\mu\text{g/L}$ and ng/L). The kinetics of SMX degradation by *A. denitrificans* compares favorably with activated sludge at the levels of ng/L (typical of wastewater) only in the presence of a supplemental C-source. It is thus concluded that co-metabolism is an important mechanism at low levels of SMX concentration ($\mu\text{g/L}$ and ng/L), particularly in the presence of acetate as C-source and energy. Regarding that acetate is an available substrate in WWTPs, these results suggest that the strain is a potentially interesting organism for bioaugmentation to achieve SMX removal.

Key Words: Sulfamethoxazole, co-metabolism, reaction rate coefficient, *Achromobacter denitrificans*

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O 4A – Evaluation of the metal/dye removal efficiency of different biomasses

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Abstract

Purpose: This study includes an evaluation of the metal/dye removal efficiency of different biomasses. The studies about removal of metal/dye with different biomasses were reviewed in this study.

Experimental description: Some of the biomasses used in the recent studies were *Lb. rhamnosus*, *Lb. 12* (Sayilgan and Cakmakci, 2013) and Lyophilized cultures of *Lactobacillus delbrueckii ssp bulgaricus*, *Streptococcus thermophilus*, and dairy mix culture of *Lactobacillus delbrueckii ssp bulgaricus* - *Streptococcus thermophilus* (Sofu et al., 2015). Generally, the biomasses are inoculated in MRS-broth under anaerobic conditions. After centrifugation, the pellets are separately collected. The dye/metal removal experiments can be conducted with synthetic and/or real wastewaters.

Results: The dye/metal removal experiments showed that the biomasses could achieve better metal/dye removal for all studies. However, the solution pH was an important factor due to the influencing the surface of biomasses. The researchers indicated that water/wastewater characterization, biomass type, biomass concentration and temperature were also other parameters could affect the removal of dye and metals (Abdel-Ghani and El-Chaghabby, 2014).

Conclusions: The removal of metals/dye with using live, dead microbial organisms, pretreated and immobilized forms of biological cells like bacteria, fungi, yeast and algae or biomass from synthetic and/or industrial wastewaters seems as an environmentally and cost-effective alternative method.

Key Words: biomass, dye, metal, removal, review

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O 5A - Perchlorate effect on ground water treatment using an ion exchange membrane bioreactor (IEMB)

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Abstract

Perchlorate contamination of ground water is a worldwide concern. At several sites in Israel's coastal aquifer, hundreds of ppm of perchlorate was found accompanied with significant concentrations of nitrate and chlorate, consequently preventing water production from wells in the area.

The IEMB hybrid process [1] allows safe treatment of high perchlorate (nitrate and chlorate) contaminated groundwater. The Donnan dialysis process removes the perchlorate from the water compartment using an anion exchange membrane (AEM). Once the perchlorate passes the AEM into the bio-compartment it undergoes microbial degradation to much safer components such as chloride ions. The AEM acts as a barrier and keeps both compartments completely separate. Glycerol is used as an exogenous carbon and electron source for the biodegradation process [2]. This arrangement keeps the carbon source, reaction byproducts and bacteria confined in the bio-reactor thus preventing the contamination of the treated water.

The present study examines the effect of treating ground water with high perchlorate concentration (100's of ppm) on the treatment process both on the AEM and on the removal efficiency of the process for the removal of other present contaminants (nitrate and chlorate).

Perchlorate was found to dominate the flux across the AEM. Even though perchlorate concentration in the water side was considerably lower than nitrate and chlorate, its flux was greater than the sum of the other anions fluxes at both experiments with and without bacteria in the bio-compartment. bacteria addition to the bio-compartment at first formed a biofilm which enhanced the total anion flux by 15- 23%, later on the biofilm growing thickness has prompt an additional resistance inevitably decreasing the flux by 18-22% as compared to a system without bacteria. Bio-molecular analysis of the bacteria in the bio-compartment has determined a spatial segregation of bacteria diversity between the biofilm (attached) and the suspended bacteria in the bio-compartment. *Klasiela oxitoca* a known glycerol fermentor was found to dominate the suspended phase of the reactor, it biochemically degrades the glycerol to a more readily carbon source. These carbon products are utilized by the abundant perchlorate reducing bacteria (PRB) identified in the biofilm for reducing the anionic contaminates.

This study is the first to treat highly polluted complex ground water in an IEMB. It further established the perchlorate strong interaction with the AEM, consequently affecting the flux of other anions in the treatment process. Additionally, the presence of bacteria in the bio-side had some beneficial effect on the flux as long as

the developed biofilm does not exceed 80 microns. This research is the basis for upscaling the IEMB technology into the field.

*Equal contribution

Key words: Perchlorate, IEMB, Groundwater

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O 6A - Impact of ship dismantling activity on the heavy metal resistance in sediment bacteria (Aliğa, Turkey)

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Abstract

Purpose: Hazardous wastes such as heavy metals and polycyclic hydrocarbons in the ship dismantling areas are accumulated in coastal sediments and lead to serious ecological problems. Since Aliğa region is the only one licensed ship dismantling zone in Turkey and the dismantling and recycling of end-of-life vessels in the zone has been identified as a key economic activity for sustainable development. But these activities have a potential to pose environmental and occupational risks. In present study, it was aimed to determine the presence and performance levels of heavy metal resistant bacteria in the zone sediments.

Experimental description: In this study, sediment samples were collected from 8 different stations in Aliğa Ship dismantling zone in 2010 by the R/V K. Piri Reis. Sediment samples were diluted and inoculated into Zobell and R2 Agar mediums. DNA isolation from different colonies was performed by using commercial kit (Zymo Research, USA). DNA sequencing (ABI Prism 3100) was performed via PCR by using universal primers and their accession numbers were obtained from NCBI. Metal resistances of these isolates were determined by minimum inhibition concentration (MIC) microdilution method and their resistances were tested against heavy metals such as Hg, Cu, Cd, Cr, Zn, Co, Ni (mM) by using Mueller Hinton medium (Kacar and Kocyigit, 2013).

Results: Phylogenetic analysis using 16S rDNA indicated that the bacterial strains belong to genus *Bacillus*. When the results of the related analysis are evaluated due to their resistance to heavy metals, it was found that their resistances can be given generally as Pb>As>Ni>Co>Cu>Zn>Cr>Cd>Hg. The highest resistances were to Pb (10mM), As (12mM) and Ni (10mM).

Conclusions: The results show that the microorganisms in the zone have been affected from the pollution like the similar organism. Inevitably, this level of heavy metal pollution causes high resistance levels in bacteria in the marine environment. In another study in this area, it was determined that the Probable Effect Level (PEL) values of the heavy metal concentrations in the sediments were higher than those of Hg, Pb, Cu, Zn and Ni in particular. Therefore, the bacterial isolates in the sediments may be used as biological indicators for the identification of heavy metal contamination at coastal areas, so bacteria should be screen their resistance and high accumulation capacities. Additionally, they could be designed as the remediation tools by further studies.

Key Words: Hazardous wastes, *Bacillus*, Heavy metal resistance, Aliğa ship dismantling zone

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O 7A – Effects of Arsenate and Arsenite on Germination and Some Physiological Attributes of Barley *Hordeum vulgare* L.

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Abstract

Purpose: In this study, we investigated the effects of various concentrations of arsenate and arsenite (0–16 mg/L) on some biochemical and physiological characteristics of barley during germination and the early stage of seedling

growth. To evaluate the toxicity of these As compounds, we determined their effects on seed germination, seedling growth (relative root and shoot lengths), α -amylase activity, reducing sugar and soluble total protein contents in root and stem tissues, and malondialdehyde (MDA) contents in barley tissues. We also quantified the As that accumulated in barley root and shoot tissues.

Experimental description: We tested the effects of arsenite and arsenate (0–16 mg/L) on seed germination, and on relative root and shoot length, α -amylase activity, reducing sugars and soluble total protein contents, and malondialdehyde content in barley seedlings. We also measured As accumulation in barley stems and roots. α -amylase activity, was determined as described by Ekinci and Aktac, (1996). Enzyme activity is expressed as units per milliliter (U/mL), as calculated from the rate of disappearance of the substrate (Ekinci and Aktac, 1996). Proteins were extracted from seeds on day 3 of the germination period using the method of Landry et al. (2001), with modifications. Protein amounts were spectrometrically measured according to Lowry method (Lowry et al. 1951). Seed germination percentages of As treated seeds were calculated relative to that of the control. The reducing sugars contents in roots and stems were measured on day 3 of the germination period using the 3–5 dinitrosalicylic acid method (Sanal et al. 2005). The thiobarbituric acid (TBA) method was used to measure MDA content, which is indicative of lipid peroxidation, in root tissues (Sun et al. 2008). Arsenic accumulation in the tissues was measured by hydride generation–atomic absorption (HG-AAS) spectrophotometry after microwave-assisted acid digestion of samples.

Results: The α -amylase activity, relative root and shoot length, and seed germination decreased with increasing concentrations of arsenate and arsenite. The reducing sugars content in barley seedlings increased after 4 days of growth on media containing As. In general, the protein content in roots and seedlings decreased with increasing doses of As. Arsenic in the tissues was quantified by hydride generation–atomic absorption spectrophotometry. To confirm the accuracy of the method, we analyzed the certified reference material WEPAL-IPE-168. The limit of detection was 1.2 μ g/L and the relative Standard deviation was 2.0 %.

Conclusions: In conclusion, barley seedlings subjected to As treatments showed oxidative stress symptoms, such as an increase in lipid peroxidation. In addition, As treatments resulted in a decrease in α -amylase activity, and changes in the reducing sugars contents and total protein contents. These biochemical changes affected the plants and inhibited their growth, depending on the As dose. These data show that barley plants can use various defense mechanisms to protect themselves against As, up to a certain critical concentration.

Key Words: Arsenite , Arsenate , Malondialdehyde ,Germination , Barley ,*Hordeum vulgare* (Sladoran)

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O 8A – Development of a new class of imprinted polymers for electrochemical sensing of organic pollutants

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Abstract

The need for efficient materials enabling selective recognition of organic molecules has led chemists to mimic biological hosts and their specific receptors based on molecular recognition. Molecularly imprinted polymers (MIPs) are designed on a similar molecular recognition process.[1] In the classical non-covalent approach, a template molecule interacts with a functional monomer and a cross-linker in a porogen solvent. After polymerization, the removal of the template generates the recognition cavities inside the three-dimensional copolymer network (Fig.1). Such materials are now widely studied as new materials for chromatographic applications, solid-phase extraction, sensor devices, in vitro diagnostic, chiral separations, catalysis and control of the biofilm formation. Their use has more recently been extended to ion templates based on similar processes.[2]

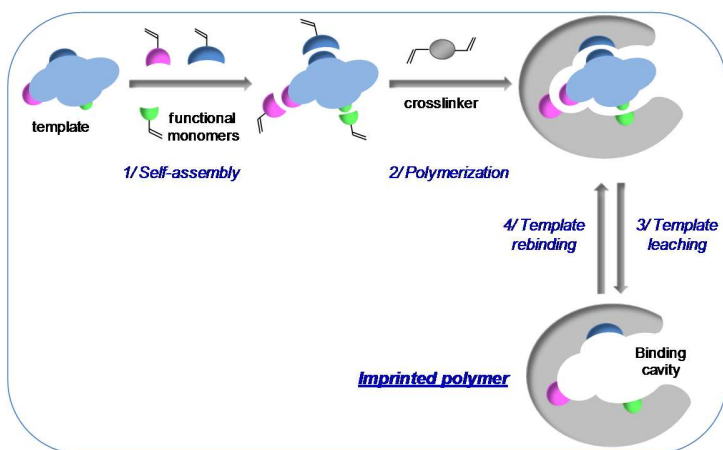


Fig. 1. Schematic representation of MIP synthesis

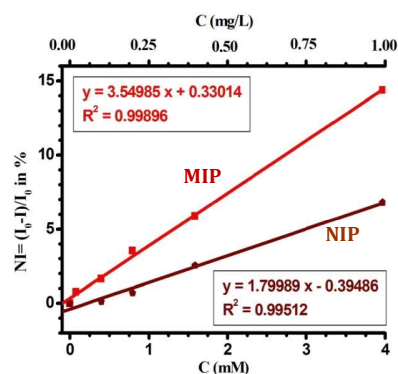


Fig.2. Normalized current curves with increasing Benzo(a)Pyrene concentrations

This talk will focus on electrochemical MIPs which have been designed to be used as the target recognition element and as part of the signal transducer in electrochemical sensors. This original approach is based on the incorporation of a redox tracer (ferrocene) as a functional monomer during the MIP synthesis.[3] Two different targets have been studied: Benzo(a)Pyrene and Bisphenol A. In both cases, MIPs were prepared by

precipitation copolymerization of a ferrocenyl vinylic monomer and ethylene glycol dimethacrylate, leading to spherical particles. The rebinding of the template by these electrochemical MIPs significantly modified the electrochemical answer of the ferrocene moiety and enabled the organic pollutant quantification (Fig.2). Those results prove that such MIPs allow the detection of non-electroactive molecules thanks to the presence of the redox tracer.

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Key Words: molecularly imprinted polymers, electrochemical sensors, Benzo(a)Pyrene, Bisphenol A

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O 9A - Linking polymer science and environmental studies: development of new specific tools for trace metal analysis.

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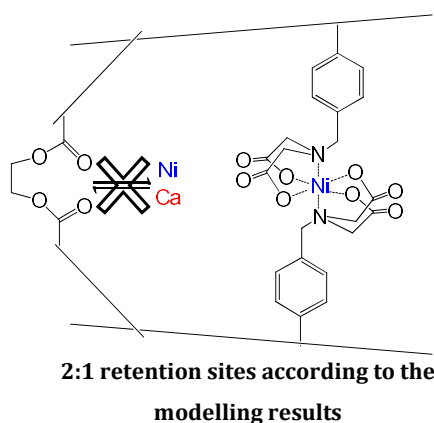
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Abstract

The presence of pollutants in worldwide ecosystems was demonstrated, very often at worrying levels. Since the last decade, the analytical improvement has led to a more accurate identification of either the organic (e.g. HAP, Bisphenol A, etc) or the inorganic (Hg, Pb, etc) contaminants. The legislative hardening all over the world has increased the traceability of the pollutant sources and their control. Yet, the protection of the ecosystems, and in a more integrative perception of Human health, depends on a proper management of the pollutants' stock. Such relevant point is depending on the precise and specific determination of contaminants. When considering inorganic contaminants, the most toxic fraction is the free (Mn+) and the labile fraction (weak complexes). The measurement of this fraction, a good indicator of the toxicity threat, can be achieved through Solid Phase Extraction, the stake being to develop a phase which is selective and precise enough.

Ion-Imprinted Polymers (IIPs) are based on a specific recognition, like a lock and its corresponding key². They can therefore be used to specifically determine a metallic fraction within a complex matrix. Ni-specific IIPs were developed and tested for their efficiency. The originality of the presented work is that IIPs were tested over a



wide range of Ni concentrations (from hundreds of $\mu\text{g/L}$ to tens of mg/L), in presence of various kinds of competitors (trace metals, major ions and organic matter) and in natural samples (seawater and freshwater). For all the tested conditions, the developed IIPs demonstrated their efficiency, even in conditions strongly in detriment of Ni retention. Finally, the processes at work were modelled, with usual polymer science methods but also classical environmental approaches, leading to a real definition of the retention site structure and properties.

Key Words: Nickel, ion-imprinted polymer, modelling, natural waters

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O 10A – Fingerprinting hydrocarbons in a contaminated soil from an Italian natural reserve and assessment of the performance of a low-impact bioremediation approach

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Abstract

Purpose. Bioremediation of organic pollutants in soil is a site-specific process, whose efficiency should be evaluated by taking into account the influence and fate of co-contaminants. A relevant protected area in the Apulia Region (SE Italy), contaminated by hydrocarbons (HC) and Cr(III), was selected as a study site. Landfarming procedures were simulated to evaluate some factors affecting the bioremediation of HC by native soil microorganisms, and the potential mobilization of chromium. In the first step of the study, the origin of soil HC was investigated through a fingerprinting study, which allowed distinguishing HC related to oil pollution (petrogenic) from natural HC produced by plants and bacteria (biogenic). Then, the most effective conditions enhancing HC biodegradation, and the potential effect of landfarming treatments on chromium mobilization were investigated. Microbiological screening by means of conventional and molecular techniques was also performed in order to characterise the soil microorganisms.

Experimental description. A sample of soil from the site was used to set up five laboratory-scale reactors simulating landfarming procedures. Before starting biodegradation tests, soil HC (C10–C40) were determined for the fingerprinting study. Chromatographic data from GC/MS analysis were used to calculate a few characteristic diagnostic indices, based on the amount ratios of selected hydrocarbon components. For the biodegradation study, each of the reactors (except the control) received a specific amendment, with the aim of enhancing biological activity. Soil in all the reactors was regularly aerated by tilling. The concentration of C10–C40 HC, Cr(III), and Cr(VI) were regularly monitored throughout 90 days.

Results. The calculation of the selected diagnostic indices led to assess that aliphatic HC in the soil were mainly of anthropogenic origin, although a biogenic component also existed. At the end of the landfarming tests, when residual HC concentration was below 50 mg kg⁻¹, the distribution pattern of HC did not show the persistence of any component of the original mixture. Degradation of HC was enhanced in the amended test reactors with respect to the control. In all cases, the maximum allowable concentration (MAC) in soil was reached within 45 days. During that time span, the amount of soil biomass did not significantly increase in all reactors. Only slight variations in the bacterial composition were observed depending on the amendment used. The concentration

of Cr(VI) was always below the MAC of 2 mg kg⁻¹, suggesting that mobilisation of chromium by oxidation of the stable form of Cr(III) to Cr(VI) did not occur in the tested conditions.

Conclusions. Fingerprinting techniques may be useful to characterise hydrocarbons contaminating peculiar sites, with a view to optimizing remediation actions. In this study, land treatment enhanced by the application of N and P amendments resulted an effective and non-invasive method to remove all hydrocarbon fractions from soil, with no effect on chromium mobilisation.

Keywords: In situ bioremediation; petroleum HC, chromium; microcosms; Fluorescent In Situ Hybridization.

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O 11A - Lung bioaccessibility of selected metals in particulate matter originating from soils and mine wastes

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Abstract

Purpose: Particulate matter (PM) from contaminated soils and mine tailings can stay suspended in air for prolonged periods, which might lead to human exposure via inhalation. The objective of the present study is to determine the lung bioaccessibility of selected metals, which is an estimation of biological availability. Bioaccessibility is determined via *in vitro* tests by measuring solubilized contaminant concentrations in synthetic body fluids.

Experimental description: Contaminated soil and mine tailings samples have been first characterized for their metal concentrations and for various physicochemical properties. *In vitro* tests for lung bioaccessibility of metals were performed using PM₂₀ (diameter <20 µm) fraction extracted from soil and mine tailings samples via micro-sieving. Bioaccessibility was determined by using two synthetic lung fluid solutions with different chemical composition and properties: ALF and Gamble's solution. Analyses were performed on liquid samples collected at different times during 2-week *in vitro* tests.

Results: Total metal concentrations were elevated in all samples, the highest ones being Fe (up to 26.3%) and Mn (7060 mg.kg⁻¹). The preliminary bioaccessibility results on two samples indicated low bioaccessibility when Gamble's solution was used, however, metal bioaccessible concentrations were high (i.e. Fe up to 7650 mg.kg⁻¹, and Mn up to 4300 mg.kg⁻¹) in the tests conducted with the ALF solution. Following the compilation of all results, we will discuss in more detail (a) the bioaccessibility of selected metals for all samples, (b) the effect of extraction time on metal bioaccessibility, (c) the performance of different tests conducted with ALF and Gamble's solutions, and (d) potential human health implications based on these results.

Conclusions: The initial results show that *in vitro* tests using Gamble's solution may underestimate lung metal bioaccessibility with respect to tests conducted with the ALF solution. Obtaining complete results will permit us to draw further conclusions, which will then be presented during our conference presentation.

Key Words: ALF solution; Gamble's solution; Heavy metals; Lung bioaccessibility; Particulate matter; Soil contamination

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O 12A – Altered vulnerability to Asthma from Airborne Polycyclic Aromatic Hydrocarbon Exposures in Children by *CTLA4*, *XPC*, and *CYP2E1* Polymorphisms

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Abstract

Purpose: 1) to clarify early-life exposures to airborne polycyclic aromatic hydrocarbons in Czech children and their role in the asthma diagnosis; 2) to estimate variability in the likelihood of asthma diagnosis according to single nucleotide polymorphisms (SNPs) per unit ambient B[a]P exposure.

Experimental description: A cross-sectional study on clinically confirmed asthmatic (n=191) versus healthy control (n=194) children (age, 7–15) was conducted by recruiting them from an industrial city and rural regions in Czech Republic. Contemporaneous exposures to ambient B[a]P at the time point of health outcome measurements were estimated based on routine, regional monitoring data for PAH data. The children's saliva DNA were genotyped for 95 candidate genes. The primary effect of B[a]P and secondary gene-environment interaction B[a]P exposure by SNPs was studied by two-stage, semi-agnostic screening of 621 candidate SNPs.

Results: Three SNPs within *CTLA4* (rs11571315, rs11571316, and rs11571319), two SNPs within *XPC* (rs2229090 and rs2607775), one SNP within *STAT4* (rs1031509), *STAT6* (rs703817), *CYP2E1* (rs2070673), and *MPO* (rs7208693), respectively were associated with significant modification of B[a]P to asthma association in the children. At highest quartile of ambient B[a]P concentration, SNPs rs11571315, rs2229090, rs1031509, and rs2070673 were associated with an elevated proportion of B/B alleles among the asthmatics compared to the trend seen in the controls. On the other hand, at the highest quartile of ambient B[a]P, the prevalence of A/A allele were highest for rs11571316, rs11571319, rs2607775, and rs703817 among the asthma- and the allergy-diagnosed, respectively. An interquartile increase in B[a]P (2.27 to 8.64 ng/m³) was associated with five-times greater likelihood of current asthma diagnosis (95% confidence interval (CI), 2.29–3.79) and five times greater likelihood of current allergy diagnosis, excluding asthma (95% CI, 1.88–2.67) after adjusting for obesity, serum cotinine, and the history of allergic rhinitis with the past 12 months.

Conclusions: Altered functions in excision repair genes, STAT and CTLA, which might render greater childhood susceptibility to B[a]P effects, require confirmation in prospective cohort study.

Key Words: Gene-Environment Interaction; Asthma; single nucleotide polymorphism; air pollution

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O 13A – Integrated processes for the recovery of valuable compounds from artichoke wastewaters

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Abstract

In recent years, the recovery of antioxidant compounds from natural sources is a focus of great interest due to their potential use as natural ingredients in food, pharmaceutical and cosmetic formulations or as substitutes of synthetic products in the food industry. The artichoke-based industry generates huge amounts of agricultural waste (up to 60% of the harvested product) consisting mainly of the leaves, stems and the external parts of the flower which are not suitable for human consumption. Blanching waters represent additional residues of the canning artichoke industry. These by-products are suitable for ensiling, with pleasant smell, good silage characteristics, crude protein content 88 g/kg, dry matter and fiber content 509 g/kg dry matter [1]. An alternative approach is their use as sources of natural antioxidant compounds, mainly phenolic compounds, which, in some cases, have activities comparable to those of synthetic antioxidants [2]. Membrane operations are recognized as powerful tools for the purification and concentration of various solutions (e.g., juices, extracts, whey) and the separation of valuable compounds from by-products of the agro-food industry. The combination of membrane processes with conventional separation technologies (i.e. adsorption, precipitation, crystallization) offers new and interesting perspectives in order to increase the selectivity of the process [3].

This work aims at giving an overview of integrated processes based on the use of membrane operations such as ultrafiltration (UF) and nanofiltration (NF) and macroporous resins, in a sequential form, for the selective purification of polyphenols with desirable bio-functional properties, from artichoke wastewater.

In particular, a preliminary UF step was investigated to remove suspended solids from artichoke wastewaters. The clarified solution was then submitted to different NF spiral-wound membranes characterized by different molecular weight cut-off (MWCO) (from 200 to 1000) and different polymeric material (polyethersulphone (PES) and polyamide (PA)) in order to produce concentrated fractions enriched in antioxidant compounds.

Finally, the NF retentate was submitted to an adsorption/desorption treatment by using three different macroporous resins based on polystyrene (LewatitS 6328 A, Lewatit S 2328 and Lewatit S 7968) in order to purify phenolic compounds, such as chlorogenic acid (CA) and apigenin 7-O-glucoside (AOG) from sugars. Samples produced in UF, NF and adsorption-desorption tests were assayed for phenolic composition (chlorogenic acid and apigenin 7-O-glucoside), sugar composition (fructose, glucose and sucrose) and antioxidant activity in order to evaluate the selectivity of each step toward compounds of interest. The performance of UF and NF membranes was also evaluated in terms of productivity (permeate fluxes) in selected operating conditions.

All the different NF membranes presented a very high retention toward phenolic compounds and TAA: no phenolics compounds were detected in the NF permeate allowing to verify the efficiency of the membrane concentration process [4]. Among the three different tested resins, the S 7968 offered the best performance in terms of adsorption/desorption ratio for chlorogenic acid, with a total adsorption/desorption yield (TADY) of 63.39%; for the apigenin 7-O-glucoside the S 7968 and the S 2328 resins showed a TADY in the range 68.31–78.45% [5]. The obtained results indicated that the integration of membrane operations with adsorbents resins can be an interesting approach for the purification of phenolic compounds from artichoke wastewaters producing a more purified fraction of phenolic compounds if compared to an integrated system fully based on the use of membranes.

Key Words: artichoke wastewaters; ultrafiltration (UF); nanofiltration (NF); macroporous resins

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O 14A – Removal of metallic pollution of waters by a thermal swing adsorption/separation process using new thermosensitive co-polymers

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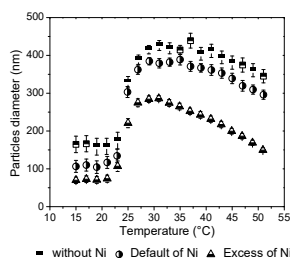
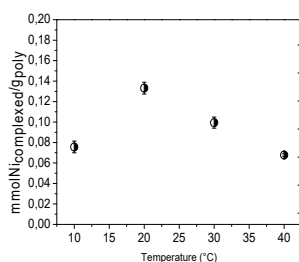
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Abstract

Purpose: Herein we propose to develop a new process to remove metallic pollution from aqueous solution combining a thermal swing sorption using new thermosensitive copolymers step coupled to a separation process.

Experimental description: new thermosensitive copolymers bearing phosphonated groups were synthesized by free radical polymerization with molar ratio hMAPC1:NnPAAm from 5:95 to 70:30. Complexing properties were brought by (dimethoxyphosphoryl)methyl 2-methylacrylate (MAPC1) monomer. N-n-propylacrylamide (NnPAAm) gives the thermo-responsive properties of the copolymers. ³¹P NMR spectrometry enabled to analyze the phosphonated groups. Sorption properties were investigated using ester cellulose dialysis membrane; the copolymer solution was immersed into a metallic solution until sorption equilibrium.

Results: Complexation properties of these copolymers toward nickel ions were evaluated for different temperature (10 to 40 °C), Ni ions concentrations of 100 mg.L⁻¹ and pH values between 3 and 7. Best results were observed for temperatures just lower than the LCST (between 18 °C and 23 °C) where the copolymer is soluble in water solution and for pH values between 5 and 7: in these conditions, more than 40 % of Ni ions were removed from solutions. Additional tests were performed in in multi-component solution of cationic species. The figures exhibit that the amount of ions sorbed by the copolymer was linked to its particle size that depended on temperature.



Conclusions: Based on a characterization of acido-basic properties of co-polymers and on the determination of particular sizes of co-polymers versus temperature, a complexation mechanism is proposed: Complexation of Ni²⁺ occurs when the copolymer was fully soluble in the solution at temperature lower than the LCST. In these conditions, best Ni complexation on the copolymer was observed for pH close to neutrality when there

was almost no competition between the sorption of H^+ and Ni^{2+} on the phosphonic acid groups. For temperature higher than the LCST, phosphonic acid groups accessibility was considerably reduced by the precipitation of the thermosensitive part of the copolymer.

Key Words: metallic pollution, sorption, thermosensitive copolymer

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O 15A - Characterisation of pseudometallophytes growing in Pb/Zn mine tailings: looking for useful bacterial inoculants for application in phytoremediation of metal-contaminated sites

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Abstract

Purpose: Mining activities are important sources of trace elements in the environment. Tailings resulting from this type of activity tend to present high concentrations of trace elements and host metal-tolerant plants, but also metal-tolerant microorganisms. The objective of this study was the establishment of a collection of metal-tolerant rhizobacteria isolates, as well as, the identification of isolates with a potential application in phytoremediation.

Experimental description: Individuals of three plant species (*Betula celtiberica*, *Cytisus scoparius*, *Festuca rubra*) naturally growing in a Pb/Zn mine in Rubiais (NW Spain) were sampled and bacteria from the rhizosphere of each plant species was isolated. Isolates were characterised for metal resistance, for the ability to produce biosurfactants, and for various plant-growth promoting (PGP) characteristics: phosphate solubilisation, siderophore production and indoleacetic acid (IAA) production. A selected group of isolates were evaluated for their influence on growth and metal uptake of plant species commonly use in phytoremediation techniques.

Results: A collection of 74 metal-tolerant rhizobacterial strains was established. Thirty eight percent of the isolates presented at least one PGP trait and/or the ability to produce biosurfactants. Twenty percent of the isolates produced biosurfactants. Fifteen percent were able to solubilise inorganic phosphate, mainly identified as members of the genera *Pseudomonas*. Only 6 strains were siderophore-producers and two were IAA-producers. The influence of 14 isolates on the growth of *Salix viminalis* and *Festuca pratensis* was assessed. Although being plant-species dependent, a total of five isolates had a positive effect on the growth of both plant species. A second experiment regarding to evaluate the effect of microbial inoculation in combination with soil amendments will be presented.

Conclusions: Metalliferous soils are not only a source of metal-tolerant plant populations, but also of metal-tolerant microorganisms that could be applied in phytoremediation trials. Isolates obtained in this study have been shown to improve plant growth of different plant species. This plant growth promotion could lead to a healthy vegetation cover in the phytostabilisation of heavily contaminated soils, or alternatively may be an important parameter in improving the metal extraction capacities of plants in the phytoextraction of metal-contaminated soils.

Key Words: phytoremediation, mining activities, plant-associated bacteria, rhizosphere

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O 16A – Qtof identification of phototransformation products of sethoxydim herbicide in water

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Abstract

Purpose: Photodegradation process is one of the most important abiotic factors affecting the fate of pesticides in aqueous systems. As consequence of this transformation pathway, different photoproducts can be formed with unknown properties such as toxicity, mobility and persistence. Therefore, information about photodegradation is essential in order to avoid underestimating the risk derived from the use of pesticides.

Sethoxydim is a cyclohexanodione herbicide and it is use for control of annual and perennial grasses in broadleaf crops. Although this herbicide is labile under sunlight, there is little research about its photodegradation mechanism and the photoproducts formed .In the present work, the photochemical fate of sethoxydim herbicide in water was studied under simulated sunlight.

Experimental description: Aqueous solutions of sethoxydim were exposed to simulated sunlight provided by Suntest CPS+ apparatus with a xenon arc lamp ($\lambda > 290$ nm). At different time intervals, aliquots were withdrawn from irradiated solutions to follow the reaction kinetics by HPLC-DAD. These aliquots were also analyzed by HPLC-ESI-QToF in order to identify the photoproducts formed.

Results: Sethoxydim was rapidly degraded in water as consequence of radiation with a half-life of nearly 1 h. A gradient HPLC method was developed in order to detect and identify the different by-products formed during the irradiation of sethoxydim. Ten by-products were detected and subsequently identified by HPLC-QToF. A detailed and exhaustive study of the mass spectra of the precursor ions and the MS/MS fragmentation patterns allowed to identify the following products: ketone derivative, imine sulphoxides, sulphoxides, imine, Z-isomer of sethoxydim and oxazole. Additionally, the reactive species involved and a plausible mechanism for the photodegradation of sethoxydim in water are discussed and a rational pathway for the photodegradation of sethoxydim in water is proposed.

Conclusions: The photolysis of sethoxydim should be considered as an efficient route of sethoxydim removal in aqueous media. The degradation products formed during sethoxydim photodegradation were identified by LC-QToF. The major photoproducts of sethoxydim formed as a result of the cleavage of the N-O bond (imine) and its corresponding oxidation product (imine ketone), both of which showed higher persistence behaviors than the parent compound.

Key Words: Sethoxydim, herbicide, photodegradation, photoproducts, QToF, photolysis mechanism.

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O 17A – Principles and Colourimetric Methods to Measure Gd³⁺ in Solution and its Complex Formation

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Abstract

Small molecule Gd³⁺-complexes have been clinically-approved as Magnetic Resonance Imaging (MRI) contrast agents (CAs) in medical diagnostic protocols to visualise a variety of physiological phenomena such as blood flow or the location of cancerous tumours.¹ Their use has been further extended as paramagnetic labels for biologically-compatible nanoparticulate and macromolecular platforms towards the synthesis of high-relaxivity MRI CAs.² However, some Gd-based agents have been implicated in the occurrence of Nephrogenic Systemic Fibrosis in renally-compromised patients,³ highlighting the need for convenient methods to detect free Gd³⁺ in solution, as well assessing completeness of Gd³⁺-complex formation in the preparation of these agents. A convenient colourimetric method involving Xylenol Orange (XO) was described as being able to detect solution concentrations of Gd³⁺ down to μM levels,⁴ and we have recently demonstrated that the origin of the sensitivity of this assay is the ion charge density of the metal ion.⁵ More recently, by taking advantage of the dramatic UV-Vis spectral/colour changes observed upon complexation of Gd³⁺ with XO, we have used the Gd³⁺-XO complex as a colourimetric probe to monitor the complex formation between Gd³⁺ and macrocyclic ligands analogous to those used clinically-approved MRI CAs.⁶ The methods described permit the facile and convenient preliminary assessment of other ligands intended for Gd-based MRI CA development.

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O 18A - Regenerable sorbents for mercury capture in simulated coal combustion flue gas

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Abstract

The impact of mercury emissions from fossil fuel combustion upon environmental pollution has been a matter of growing concern in recent years. Coal combustion power plants are the largest anthropogenic source of mercury emissions [1]. Mercury released by burning coal is converted into a far more toxic form when it enters the food chain. For all these reasons several governments, organizations and scientists worldwide are working to limit mercury emissions, including those produced by coal combustion. In the last session of the UNEP (United Nations Environment Programme) held in 2013 in Minamata, Japan[2], the "Minamata Convention on Mercury" established eight priorities for action which reflect the main mercury emission sources. One of these priorities was "Mercury emissions from coal combustion"

Activated carbons are extensively used by many researchers for mercury retention in coal combustion and incineration process [3]. However, the use of these adsorbents in coal combustion plants has certain limitations related with particulate control devices and the reutilization of fly ash, as well as their cost. An attractive option for reducing the emissions of Hg⁰ is the use of regenerable sorbents since this avoids the generation of toxic waste. The aim of this study is to evaluate the retention of mercury by sorbents consisting of an activated carbon loaded with gold nanoparticles and its regeneration.

The experiments were carried out in a laboratory-scale reactor in a simulated flue gas of coal combustion. The mercury content of the sorbent after retention was determined by means of AMA equipment, whereas the Hg⁰ not retained in the sorbents was controlled by means of a continuous mercury monitor (VM-3000). The effect of multiple regeneration cycles on the lifetime of the sorbent was evaluated by heating the post-retention sorbent in the same experimental device from room temperature to 550 °C.

The dispersion of gold nanoparticles was found to be highly effective for mercury capture using 5% gold-doped regenerable sorbents. The sorbent was thermally regenerated at approximately 240 °C and the Hg⁰ was recovered and collected in a container. An approximate initial cost analysis showed that a high level of investment due to the cost of gold must be made. However, the gold can be recovered. Therefore, the proposed sorbent could be an efficient method of mercury capture in power plants without generating new toxic waste.

Key Words: mercury, coal combustion, regenerable sorbents

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O 19A – Application of waste-based adsorbents for the removal of pharmaceuticals from contaminated water

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Abstract

Purpose: This work aims to produce alternative adsorbents, recurring to sustainable methodologies and using as starting materials sub-products of the paper mill industry, for application in the treatment of effluents contaminated with pharmaceuticals. The adsorbents are aimed to have an efficiency/cost ratio competitive with the commercially available activated carbons, allowing its generalized application at much lower costs.

Experimental description: Alternative adsorbents were produced by the controlled pyrolysis of primary and biological paper mill sludge. Physico-chemical characterization of the adsorbents was performed by elemental and proximate analyses, total organic carbon, specific surface area (BET), N₂ isotherms, FTIR, ¹³C and ¹H solid state NMR and SEM. The performance of the adsorbents on the removal of pharmaceuticals from water was tested by a batch experimental approach that included kinetic and equilibrium experiments. All these experiments were also performed using a commercially available activated carbon for comparison purposes.



Results: The best adsorbents were obtained from the pyrolysis of primary paper mill sludge. The production process effectively resulted in the disappearance of the main functional groups of the starting material, generating highly aromatic structures with a well-developed microporosity and a high specific surface area. The adsorption kinetics of the tested pharmaceuticals onto the produced materials is almost instantaneous (a few minutes), which constitutes an interesting feature considering their hypothetical application in waste water treatment plants.

Conclusions: The use of pyrolysed paper mill sludge for the remediation of contaminated waters might constitute an interesting sustainable solution for water remediation and also an alternative way for the valorization of these wastes. The produced materials are currently being tested under continuous operation mode in order to further investigate their applicability as adsorbents in real waste water treatment systems.

Key Words: Waste water treatment; Water remediation; Adsorption; Pyrolysis; Paper mill sludge.

Acknowledgements: This work was supported by European Funds through COMPETE and by National Funds through the Portuguese Science Foundation (FCT) within project PEst-C/MAR/LA0017/2013. V. Calisto and C.I.A. Ferreira thank FCT for their postdoctoral (SFRH/BPD/78645/2011) and PhD grants (SFRH/BD/88965/2012), respectively. V. Calisto also thanks funding from the L'Óreal Foundation through the Honor Medal for Women in Science 2014.

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O 20A – Effects of a sulfonylurea herbicide on the soil bacterial community

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Abstract

Purpose: In this study, we hope to characterize the soil bacterial community before and after treatment with the Chevalier® OnePass herbicide which is a sulfonylurea herbicide intensively used on cereal crops in Algeria. We focus also to study the biodegradation of this herbicide or about its effect on the bacterial community of the soil.

Experimental description: We collected an untreated soil sample, and another sample was collected 1 month after treatment with the herbicide. We first confirm the presence of the herbicide in the second soil sample using an ICP Technique. Using a high-resolution melting DNA technique, we show the effect of the herbicide on the bacterial community. We then determine the ability of bacterial strains isolated from the soil, before and after treatment, to degrade the herbicide using an overlay culture technique.

Results: We have shown that treatment with Chevalier® OnePass herbicide only slightly changed the composition of the whole bacterial community. Surprisingly, we found that among ten strains isolated from the treated soil, only six were resistant to the herbicide. Furthermore, bacterial overlay experiments showed that only one resistant strain (related to *Stenotrophomonas maltophilia*) allowed all the sensitive strains tested to grow in the presence of the herbicide.

Conclusions: On the basis of these results, we propose that there must be several biodegradation pathways for this sulfonylurea herbicide.

Key Words: Sulfonylurea . Chevalier® OnePass herbicide. Soil bacterial community. High-resolution melting DNA . Bacterial overlay cultures.

Acknowledgements: We would like to thank A. Rouabah for his help in the soil sample collection and V. Michotey for supplying the oceanic metagenome. This work is funded by the Faculté des Sciences de la Nature et de la Vie, Université Constantine 1 (Algeria), the Centre National de la Recherche Scientifique (CNRS), and the Aix-Marseille Université (France).

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O 21A – Restricted access supramolecular solvents in chiral environmental analysis

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Abstract

Supramolecular solvents (SUPRAS) are water-immiscible nanostructured liquids consisting of three-dimensional amphiphile aggregates able to solubilize a wide variety of solutes because of the different interaction mechanisms (dispersion, dipole-dipole, hydrogen bond, etc.) they provide and the high amphiphile concentration ($0.1\text{--}1\text{ mg L}^{-1}$) and hence, of solubilization sites, they possess. In addition, SUPRAS synthesized in ternary mixtures of alkyl carboxylic acid, tetrahydrofuran (THF) and water consisting of inverted hexagonal surfactant aggregates have restricted access properties excluding macromolecules (i.e. proteins, humic and fulvic acids and polysaccharids) through both physical and chemical mechanisms. Therefore, these restricted access solvents (SUPRAS-RAM) permit to extract small molecules and exclude macromolecules from samples in a single-step, providing cleaner extracts than those obtained using organic solvents. Investigations performed by our research group on SUPRAS-RAM have demonstrated that the special features of these solvents make them excellent extractants in analytical process and that their use allows the simplification of sample treatments in complex analysis.

This work presents research results from studies on the utilization of SUPRAS-RAM in chiral environmental analysis. Difficulties for the enantioselective determination of chiral contaminants include great similarity between the molecular structures of enantiomers, low concentration of the analytes in samples and complexity of environmental matrices. The few methods reported for enantiomer quantitation in these matrices usually involve several extraction steps, clean-up and concentration of extracts and separation and quantitation of the enantiomers by gas or liquid chromatography (GC or LC) coupled to mass spectrometry (MS).

Major benefits of using SUPRAS-RAM in chiral analysis includes fast and simultaneous analyte extraction and sample cleanup (5-10 min), use of conventional equipment, and the possibility of treating several samples simultaneously. SUPRAS-RAM-based extractions have been applied to the quantitation of the R and S enantiomers of mecoprop (MCP) and diclorprop (DCPP) in natural waters and soils, the R and S enantiomers of ibuprofeno (IBP), ketoprofen (KTP) and naproxen (NPX) in waste waters and fresh fishes, and the stereoisomers of hexabromocyclododecane (HBCD), (+)- and (-)- α -HBCD, (+)- and (-)- β -HBCD and (+)- and (-)- γ -HBCD, in soils, sediments and fishes prior to their quantification by chiral LC-MS. The high extraction efficiencies of SUPRAS-RAM resulted in high concentration factors for aqueous samples (94-700) and high recoveries for the solid ones (80-100%) using low SUPRAS volume/sample amount ratios ($0.6\text{--}1.7\text{ }\mu\text{L mg}^{-1}$).

Quantification limits at the low ng L⁻¹ and ng g⁻¹ level for aqueous and solid samples, respectively, were provided by all developed methods.

Key Words: Supramolecular solvents; Restricted access solvents; Chiral analysis; Liquid chromatography/tandem mass spectrometry.

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O 22A - Effects of rapeseed oil on the rhizodegradation of polyaromatic hydrocarbons in contaminated soil

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Abstract

Purpose: The aim of this study was to investigate the influence of vegetable oil as soil amendment on the rhizodegradation of PAHs in the soil from a historically contaminated site.

Experimental description: Two experiments were performed: (i) a classical pot experiment with five different plant species to investigate the effect of plants and vegetable oil on the soil PAH content and (ii) a rhizobox-experiment that facilitates the measurement of PAH contents in small distances from the plant roots.

Results: The results suggested a significant impact of vegetable oil (1 and 3 % w/w) on plant growth (decrease of plant height and biomass). The results of the pot experiment showed a decrease in the PAH content of the soil without amendment of rapeseed oil after six months. In soil amended with 1 % and 3 % of oil, there was no decrease in PAH content within this period. Although no enhancement of PAH degradation by plants could be measured in the bulk soil of the pot experiments, a rhizobox experiment showed a significant reduction of PAH content in the rhizosphere of alfalfa (*Medicago sativa* cv. Europe). Our investigations also showed significant differences in the degradation behaviour of the 16 individually analysed PAHs.

Conclusions: Our results show that in any in-situ application of vegetable oil for soil remediation the interaction of the phase mixture oil-water-air in soil with microorganisms and plant roots have to be considered very carefully to prevent biological impairments.

Key Words: phytoremediation, rhizosphere, in-situ remediation, vegetable oil

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O 23A – Remediation of Chromium-Polluted Soil by Phytoextraction: Factors and Conditions for Using *Portulaca oleracea*

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Abstract

Phytoextraction is a technique used to remediate contaminated soil or water using plants which are cable to extract the pollutants from the soil by the roots and then it translocates and accumulates them in the above-ground parts of plant, such as shoots, leaves and stems. The plant is then harvested and disposed in a safe and contained environment. We have reported recently [1,2] that *Portulaca oleracea* has been shown to be an excellent candidate for Cr(VI) accumulation from contaminated soil, where more than 95% of the accumulated Cr(VI) was reduced to the less toxic Cr(III) within the plant. The uptake of the heavy metal by the plant is significantly affected by different factors including, concentration of metal, pH, concentration of organic matter, and the presence and concentration of other metals and anions. In this paper, we present the results of a study conducted on the uptake of Cr(VI) by *Portulaca oleracea* under different conditions and factors. The results of these investigations will be presented and a set of optimized factors will be recommended.

Key Words: phytoextraction; *Portulaca oleracea*; chromium; soil contamination; heavy metals.

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O 24A - The effects of BaSO₄ loading on OPC cementing system for encapsulation of BaSO₄ scale from oil and gas industry

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Abstract

Purpose: The BaSO₄ scales obtained from piping decontamination from oil and gas industries are most often classified as low level radioactive waste. These wastes could be immobilised by stable cement matrix to provide higher safety of handling, transportation, storage and disposal. However, the information available for the effects of the basic formulation such as waste loading on the fundamental properties is still limited. The present study investigates the effect of BaSO₄ loading, particle size and water content on the phases, microstructure and compressive strength of OPC–BaSO₄ systems.

Experimental description: Simulated wasteforms have been produced using ordinary Portland cement with BaSO₄ in the fine powder and coarse granulated forms, at different level of BaSO₄. In addition the w/c ratio was altered to reflect the change in the water content when adding an inert solid to cement. TG, XRD and mechanical testing were used to characterise the products, to determine an acceptable loading and mix formulation, and establish whether large amounts of BaSO₄ may be encapsulated in cement.

Results: Both in OPC–BaSO₄ powder and OPC–BaSO₄ granule systems, it was possible to produce solid products containing up to 60 wt% of BaSO₄ loading which satisfies the minimum compressive strength of 5 MPa required for the radioactive wasteforms. The fine BaSO₄ powder caused an increased formation of CaCO₃, which appeared to increase the compressive strength of the products. The strength decreased with the BaSO₄ granule contents to approximately 20 MPa for w/c = 0.53 series and around 10 MPa for w/s = 0.53 series, but did not change significantly with a further increase in the BaSO₄ granules. The ncrease in water resulted in the increase in porosity of products, which was more significant in the OPC–BaSO₄ powder system. There was no significant difference in porosity between BaSO₄ powder and BaSO₄ granule systems when w/c was 0.53.

Conclusions: It was possible to achieve high BaSO₄ loadings whilst retaining the initial integrity of the wasteform products. It would be beneficial to incorporate small amount of fine BaSO₄ powder about 12 wt% to maximise the strength of the product if the formation of CaCO₃ in the product is not an issue. BaSO₄ may be further incorporated, in the form of coarse granule to give a total of 60 wt% without reducing the strength of the product drastically. It is important to maintain w/c ratio at around 0.53 to maintain the low level of porosity in the final waste product.

Key Words: BaSO₄, oil scale, Portland cement, mechanical strength, carbonation

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O 25A – Impact of Zn-Pb mining in the Olkusz ore district on the Permian aquifer (SW Poland)

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Abstract

Purpose: The purpose of a study was to investigate changes in chemical compositions of waters within Permian sediments that underlay a Zn-Pb deposits of Triassic age near Olkusz in southern Poland during exploitation of Pomorzany mine.

Experimental description: Water samples were collected in the period from 1970 to 2011. Nearly 200 samples were collected mostly from inflows and seepages occurring in shafts and drifts excavated in Permian conglomerates. Samples were also collected from exploratory boreholes drilled during deposit documentation and exploration stages, piezometers and wells located in investigated area. Unfortunately, in many samples only selected parameters were determined, thus the number of useful results is smaller (about 170). All sample were analysed in a Hydro-chemical Laboratory of Department of Hydrogeology and Engineering Geology, AGH University in Krakow, Poland. Standard analytical methods were used.

Results: At the initial stage of Pomorzany mine development it was observed that with increasing depth, measured from the roof of Permian conglomerates, TDS increased. Vertical hydro-chemical zonality was also observed. Along with increase in TDS hydro-chemical type of water started to change. Water with TDS of single grams per litre showed tendency toward decreasing mineralization in zones of fissures or small faults. During a development stage of Pomorzany Mine the waters from inflows presented TDS from 0.38 g/L to 0.59 g/L and belonged to general type $\text{HCO}_3\text{-Ca-Mg}$ and $\text{HCO}_3\text{-SO}_4\text{-Ca-Mg}$. Water samples collected from inflows in this area in years 1996-2010 (after at least 25 years of intensive mining drainage) presented completely different chemical composition. TDS ranged from 1.47 g/L to 5.14 g/L and chemical type of waters has changed to $\text{Ca-Mg-SO}_4\text{-HCO}_3$ or $\text{SO}_4\text{-Ca-Mg}$ and $\text{SO}_4\text{-Mg-Ca}$.

Conclusions: Long-term extensive mining of Zn-Pb ores in the Olkusz area resulted in significant changes of water table levels and affected chemical composition of water in all aquifers in the area. Within Permian aquifer hydro-chemical type of water evolved in two general stages. Short-term effect was freshening in the zones of contact with overlying Triassic limestones and dolomites. Long term effect was a change in flow pattern and, as a consequence, an inflow of naturally altered, and additionally anthropogenically contaminated water from Triassic aquifer into Permian sediments (conglomerates). This was especially intensive in densely fissured and fault zones.

Key Words: Zn-Pb ore mining, Olkusz region, neutral drainage

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O 26A – Can hybrid larch be a relevant choice for cadmium phytoextraction?

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Abstract

Tree species are considered as new tools for phytoextraction of trace elements (TE) because of their high biomass and their deep root system. Among them, Gymnosperms are not widely used despite several species could be as efficient as Angiosperms on cold and dry areas [1-3]. Therefore, we investigated the capacity of a hybrid larch (*Larix x eurolepis* Henry) to accumulate Cd. The study was performed with somatic embryos and Cd exposure was tested on one-month-old *in vitro* grown plantlets. *In vitro* screening is an interesting first step for several reasons: 1) growth rate is higher than under natural conditions, 2) TE availability is higher in culture medium accelerating their uptake and decreasing the time of exposure and 3) required space for experiments is smaller [4].

In a first attempt, one-month-old plantlets were transferred for one week on new media containing 0 or 1.5 mM Cd. Results showed that biomass was similar to control plantlets and shoot Cd concentration was higher than 100 mg. kg⁻¹ dry weight, the minimum shoot concentration to qualify a hyperaccumulator [5]. However, growth stopped after two-week treatment, indicating a probable long term toxicity with this high Cd concentration.

In a second step, larch plantlets were exposed to lower Cd concentrations (0.25 and 0.5 mM) for 2 to 4 weeks. Plantlets exhibited a significant growth reduction after 4 weeks on 0.5 mM Cd but they looked still healthy on 0.25 mM. For this latter concentration, photosynthetic pigment and total soluble carbohydrate contents remained unchanged compared to control. Total soluble amino acid concentration slightly decreased but we recorded a slight increase in total soluble proteins, suggesting that plantlets may enhance defense mechanisms. Moreover, proline content in shoots was higher than in control, confirming the stimulation of defense pathways, as proline is known as an osmoprotectant and an anti-oxidative compound. In parallel, the level of thiobarbituric acid reactive substances was not modified, suggesting that plantlets did not undergo lipid peroxidation.

After 4 weeks on 0.25 mM Cd, plantlets stored more Cd in roots than in shoots, what is often observed even for Cd hyperaccumulating species. However, shoot Cd concentration remained higher than 100 mg. kg⁻¹ dry weight and the ratio shoot / root for total Cd accumulated per plantlet was close to 1, indicating an efficient Cd translocation to aerial parts. Synthesis of cysteine-rich molecules such as phytochelatins (known to bind Cd *via* thiol functions) was not stimulated, suggesting another way of Cd scavenging that we have to investigate.

Nevertheless, high level of Cd in aerial organs is promising and allows us to defend hybrid larch as a good potential Cd phytoextractor.

Keywords: Conifer, phytoaccumulation, phytoremediation, somatic embryogenesis

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O 27A - Toxicity of vanadium on isolated rat liver mitochondria: a new mechanistic approach

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Abstract

Purpose: Vanadium as a trace element is considered essential for animals; however it has not yet been recognized as a micronutrient for humans. Most of the information on the biological effects of vanadium was related to metal's insulin-like, anti-hyperlipidemic and anticancer properties in low concentrations. According to the previous literature, mitochondria were proposed as an important target for vanadium cytotoxicity. In this study, the mitochondrial toxicity mechanisms of sodium metavanadate (vanadium V or V5+) were investigated in the isolated mitochondria obtained from rat liver.

Experimental description: isolated mitochondria obtained from rat liver by differential centrifugation and mitochondrial toxicity endpoints as well as mitochondrial sources of ROS formation were determined in both in vivo and in vitro using specific substrates and inhibitors. For in vivo studies first, single injection of V5+ at different concentrations of (10, 20 and 40 mg kg⁻¹, i.p.) was applied into Wistar rats. On the other hand for in vitro studies different concentrations of V5+ (25, 50, 100 and 200 mM) were directly added on liver mitochondria isolated from Wistar rats.

Results: Single injection of V5+ into Wistar rat (10, 20 and 40 mg/kg, i.p.) caused a significant increase in serum alanine aminotransferase (ALT) and aspartate aminotransferase (AST) levels. Isolated mitochondria from the V5+-treated rat liver showed a marked elevation in oxidative stress parameters accompanied by mitochondrial membrane potential (MMP) collapse as compared to a control group. On the other hand, our in vitro results with isolated mitochondria showed that different concentrations of V5+ (25–200 mM) induced significant ($P < 0.05$) progress in mitochondrial ROS formation, ATP depletion, GSH oxidation, mitochondrial outer membrane rupture, mitochondrial swelling and cytochrome c release before the mitochondrial potential collapse ensued. We also showed that the V5+ interaction with respiratory complex III is the major source of V5+-induced ROS formation.

Conclusions: In general, our in vivo and in vitro data strongly supported that the V5+-induced liver toxicity is a result of the metal disruptive effect on the mitochondrial respiratory complexes I, II and III which are the obvious causes of metal-induced ROS formation and ATP depletion in liver cells which leads to cell death signalling via MPT pore opening and cytochrome c release.

Key Words: vanadium (5+); mitochondria; complex I; Complex III; Reactive Oxygen Species (ROS); mitochondrial permeability transition (MPT); Liver toxicity.

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O 28A – Rapid and sensitive determination of polycyclic aromatic hydrocarbons at trace levels in aqueous samples using RP-HPLC with a fluorescence detector

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Abstract

Purpose: In this work, a fast and simple analytical methodology for the separation and quantification of anthracene (AN) and benzo(a)pyrene (BaP), two of the most priority PAHs for their photoinduced toxicity and carcinogenic associated character, respectively, at trace levels in aqueous samples by direct injection is optimized and validated.

Experimental description: PAH analysis was carried out using a reverse phase high performance liquid chromatography (RP-HPLC) system with a fluorescence detector (FLD). Statgraphics Centurion XVI program package was used for data statistical treatment and a fractional factorial and a Box-Behnken experimental design was chosen for screening and multiresponse optimization purposes, respectively.

Results: The optimized parameters influencing significantly the system (with a 95% of significant level), from those screened for a run total time of 5 min, were: a) flow speed (1 mL/min), b) strength of the mobile phase (90% of acetonitrile:10% Milli-Q water), c) column temperature (35 °C) and d) excitation wavelength (254 nm for AN and 267 nm for BaP, respectively). The injection volume was fixed at 100 µL and the emission wavelength at 416 nm. The quantification limit was found to be 75 and 30 ng L⁻¹ for AN and BaP, respectively, and the coefficients of variation for the intra- and inter-day precision were < 20%.

Conclusions: The proposed analytical method enables to determine in aqueous samples with a good resolution and in a fast and easy way levels of AN and BaP below those allowed in the recently launched and more stringent Directive 2013/39/EU in the field of water policy. Additionally, this work shows the guidelines to be followed for the development of analytical methodologies optimizing simultaneously several response factors using experimental designs.

Key Words: Polycyclic aromatic hydrocarbons; RP-HPLC-FLD; multiresponse optimization; Box-Behnken design

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O 29A – On the effects of the dispersant corexit 9500 during the degradation process of N-alkanes and PAHS in marine Sediments

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Abstract

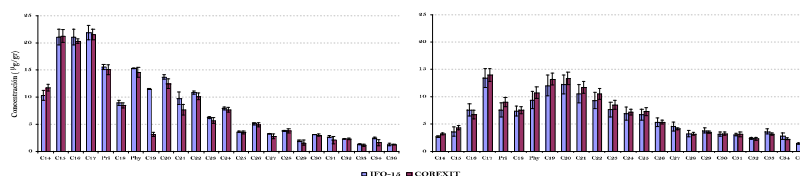
In many countries, oil spill contingency plans include dispersant as alternatives for removal of spilled oil from the ocean. Because this process applies chemical substances that may add toxicity to oil that already contains toxic compounds, it is, at times, a controversial method to fight oil pollution. Additionally, local conditions may result in particular complications. We investigated the possible effects of the dispersant Corexit 9500© under conditions similar to those of subtropical oceans. We used fuel oil #6 + diesel as the test mixture. Under certain conditions, at least part of the dispersed oil may reach the sediment, particularly if the dispersant is applied in coastal waters.

Purpose: The purpose of this work was to determine what the effect would be, if any, by the presence of the commercial dispersant Corexit 9500© on the degradation process for n-alkanes and PAHs when these mixtures are combined in seawater and, in particular, in sediments at typical subtropical temperatures and salinities. Although one particular formulation was used, this study may still be applicable to other oil mixtures of similar formulations.

In the case of spills in Mexican coastal waters contemplate the use of these substances, and we wanted to contribute relevant information on the potential of these commercial formulas to work under subtropical conditions.

Experimental description: The experimental set up included nine glass contains, all under the same conditions of temperature, salinity, air fluxes and the hydrocarbon concentration (IFO-15). The experiment consisted of two treatments and one Control (C), each with three replicates. These units were randomized to avoid bias and diminish demonic intrusion. Gas chromatography was used as a method of quantifying

Results: The results of this experiment show what would be expected of an ageing of the n-alkanes under normal conditions in the environment. That is, the shift in the maximum of the concentration for the alkanes, in our case from around C-15 or C-16 to C-19 or C-20 at the end of the experiment as shown below:



Conclusions: We found not too many benefits in using Corexit 9500© in applications near the coast as far as degradation is concern. It appears to have limited effects on the degradation for both n-alkanes and PAHs. The only benefit would be the fact that visually, most of the crude would disappear from the surface into the water column, thus decreasing the visual impact on the coastal communities.

Key Words: Oil spills, dispersants, Corexit 9500©, marine sediments.

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O 30A – Electrochemical wastewater treatment: Influence of the type of carbon and of nitrogen on the organic load removal

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Abstract

Purpose: The aim of this work was to study the electrodegradation of humic acid, a persistent organic pollutant present in wastewaters, in the presence of different combinations of organic and inorganic species, and to determine the influence of the solution's composition on the electrodegradation process.

Experimental description: The anodic oxidation assays were performed using two different anode materials, BDD and Ti/Pt/PbO₂. The synthetic samples were prepared as aqueous solutions of humic acid with different contents in organic and inorganic carbon and nitrogen compounds, namely K₂CO₃, C₆H₁₂O₆, (NH₄)₂SO₄ and (NH₂)₂CO. The influence of chloride ion was also assessed, by adding KCl to the synthetic samples. Experiments were conducted in batch mode, with stirring, using 200 mL of solution, at an applied current density of 700 A m⁻². Assays were followed by chemical oxygen demand (COD), total dissolved carbon (TDC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and total dissolved nitrogen (TDN) determinations. The Cl⁻, ClO₃⁻, ClO₄⁻, NO₂⁻, NO₃⁻ and NH₄⁺ concentrations were also determined by ion chromatography.

Results: Results indicated that, for the experimental conditions assayed, the presence of CO₃²⁻ in solution is beneficial for the organic nitrogen removal, although it hinders the oxidation of the carbonaceous organic matter. Organic nitrogen is oxidized to NH₄⁺, which in turn is oxidized to nitrate and to volatile nitrogen compounds, being the oxidation to nitrate favored by BDD, and the oxidation to volatile nitrogen more likely when the Ti/Pt/PbO₂ anode is used. The presence of chloride enhances COD, DOC, TDN and NH₄⁺ removal rates, indicating that the indirect oxidation of humic acid through chlorine/hypochlorite species occurs in parallel to the indirect oxidation through hydroxyl radicals, especially in the presence of CO₃²⁻, and that the NH₄⁺ removal occurs mainly through the chlorine/hypochlorite species. BDD anode yields the highest COD, TDC, DOC, TDN and NH₄⁺ removals, especially when chloride is present. Moreover, it is more oriented towards the oxidation of DOC to DIC. Ti/Pt/PbO₂ is very effective on the Cl⁻ removal, oxidizing it to ClO₃⁻, especially in the presence of nitrogen-containing species.

Conclusions: The knowledge of the influence of the different species and anode materials on the electrooxidation process has a high practical relevance as it can be used to select the optimum operational conditions. The obtained results indicate that, besides chloride, the presence of carbonate ion has also an important influence on the electrooxidation process. Despite BDD yielded the highest removal rates, Ti/Pt/PbO₂ showed to be a promising material for the electrochemical wastewater treatment.

Key Words: persistent organic pollutants; humic acid; electrochemical treatment; anodic oxidation; BDD anode; Ti/Pt/PbO₂ anode

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O 31A - 2,2'-dipyridyldisulfide, one of the metal pyrrithione degradation products; toxicity to a marine fish and induction of notochord undulation and skeletal deformities

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Abstract

Purpose: Copper pyrrithione and zinc pyrrithione are used as alternative antifouling paint biocides to organotin compounds in Japan. Both metal pyrrithiones (MePTs) are easily photolyzed and are thought to readily degrade to nontoxic products in the natural environment. However, we detected one of the degradation products of MePT, 2,2'-dipyridyldisulfide [(PS)₂], in a seawater sample. This finding suggests that (PS)₂ is more stable than MePT and highlights the urgency and importance of assessing the ecological risk of (PS)₂ to marine organisms. In this study, we investigated the toxicity of (PS)₂ to marine fish, *Fundulus heteroclitus*, and the mechanisms of notochord undulations and skeletal deformities induced in the (PS)₂-exposed fish.

Experimental description: The early-life stage (ELS) test were carried out with geometric series of nominal (PS)₂ concentrations that varied by factors of 3 from 3 to 243 ug/L, respectively. In ELS test, embryos were exposed for 50 days, and hatchability and growth were measured. Embryo toxicity test was also carried out and lysyl oxidase activities in exposed and non-exposed embryos were measured according to Anderson et al. (2007). Runx2 cDNA was cloning from total RNA in embryos and its mRNA were measured using real-time quantitative PCR.

Results: In the ELS test, hatchability and survival were lower in the 81- and 243-ug/L group, respectively. The LOEC and NOEC (endpoint, growth) in light of the actual concentration were 16.7 and 5.9 ug/L, respectively. In 243-ug/L group, morphological deformity of the notochord was observed for more than 80% of the hatched larvae. The shape of vertebrae around the bent region was not uniform and sometimes the region lacked vertebrae. In embryo toxicity test, lysyl oxidase activity of the exposed embryos in gastrulae stage was significantly decreased. Molecular cloning of Runx2 cDNA was carried out and its expression was characterized during embryogenesis. Although expression levels of non-exposure embryos were higher in blastula, gastrula and organo-differentiation stages, the Runx2 mRNA expression in exposed embryos was not changed.

Conclusions: These results suggest that (PS)₂ has the toxicity to *Fundulus heteroclitus*, which is characterized by the inhibition of lysyl oxidase activity in gastrulae embryos and the induction of notochord undulations.

Key Words: antifouling biocide, (PS)₂, Lysyl oxidase, Runx2, notochord undulation, skeletal deformity

Acknowledgements: We are grateful to Ms. Chiaki Hiramoto.

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O 32A – Chronic exposure to non-eruptive volcanogenic air pollution as cause of lung injury

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Abstract

Purpose: Despite the fact that several pathologies of the respiratory tract have been associated with exposure to air pollutants of anthropogenic origin, few studies have been made regarding the exposure to volcanogenic air pollution, representing an unrecognized health risk for humans inhabiting non-eruptive volcanically active areas. In this study tested the hypothesis whether air pollution of volcanogenic origin causes lung injury using wild mice as surrogate species.

Experimental description: The extent of lung injury was assessed by studying the following histological morphometric parameters: percentage of alveolar space (PA_{lvS}), alveolar perimeter (AlvP) and septal thickness (AlvST). By using these parameters a lung structural functionality ratio was also determined. The inflammatory status (InfS) and amount of black silver deposits (BSD) within the lung tissue were also considered in the evaluation of lung injury.

Results: We found that mice exposed to air pollution have decreased percentage of alveolar space (PA_{lvS}), alveolar perimeter (AlvP) and lung structural functionality ratio (LSF) and, increased alveolar septal thickness (AlvST), amount of black silver deposits (BSD) and InfS. For the first time, we present evidence of these effects in individuals living in a volcanically active environment.

Conclusions: Globally, our results clearly show that non-eruptive active volcanism has a high potential to cause lung injury in individuals chronically exposed. We also highlight the usefulness of *M. musculus* as bioindicator species, and of the developed biomarker of effect LSF ratio, for future animal and/or human biomonitoring programs.

Key Words: Air pollution, lung structural functionality ratio, mice, pulmonary inflammation, volcanism.

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O 33A – Toxic molecules in the aerosol particulate matter in Lombardy region (Northern Italy)

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Abstract

Purpose: Air pollution is now the world's largest single environmental health risk and can cause a variety of environmental effects also on ecosystem and cultural heritage. The air pollution situation is not moving forward and research is very much needed. Well known pollution sources (e.g. traffic, biomass burning) and new drivers (e.g. new sources, fast urban development) bring new challenges. Aerosol particulate matter (PM), together with gases (e.g. NO_x, PAH, VOCs, SO₂), are the main responsible for atmospheric pollution and its effects. In this context, a detailed chemical characterisation of particulate matter is needed to identify pollution sources and assessing the environmental impact. The main aim of the present work is the characterization of a large number of species in the aerosol particulate matter collected in two kinds of sites, one urban and one rural, representative of the typical atmospheric pollution encountered in the Lombardy region, northern Italy.

Experimental description: This work is focused on PM₁₀ samples collected in two representative sites of the Air Quality Network (AQN) of Lombardy: the urban background site of Milano-Pascal and the rural site of Corte de Cortesi, characterized by agricultural and zootechnical activities from the southern part of the region. Different classes of substances were determined starting from the main PM constituents such as anions (SO₄²⁻, NO₃⁻, Cl⁻) and cations (Ca²⁺, NH₄⁺, Mg²⁺, K⁺), organic and elemental carbon (OC and EC) and elements with Z>11 by X-ray fluorescence spectroscopy (XRF). Furthermore, some classes of organic molecules, characterized by toxic effects on human health, were quantified as well: polycyclic aromatic hydrocarbons (PAH's), polychlorinated dibenzodioxins and polychlorinated dibenzofurans, all recognized as carcinogenic by IARC (International Agency for Research on Cancer), and also aliphatic amines.

Results: The data acquired over one year allowed the quantification of the main PM sources. In particular, the contribution of traffic, biomass burning and secondary origin molecules (ammonium sulphate and nitrate) have been highlighted in the urban site. As concerns the rural site the main sources identified are represented by biomass burning and secondary origin molecules. PAH's in the particulate phase increase during the winter period, reaching the maximum value in December when biomass burning is the main source for the entire Po Basin. Dibenzodioxins and dibenzofurans are also associated with biomass burning and maximum values have been registered during fires. In both urban and rural site aliphatic amines (DMA, EA, TMA and DEA) have been identified with higher concentrations in the rural site. These substances, associated mainly to animal feeding operations, are present in the gas phase but are also subjected to gas-to-particle conversion reactions.

Conclusions: Aerosol particulate matter contains some classes of substances (such as PAH, amines, dibenzodioxins and dibenzofurans) that have been recognized as toxic for human health. The air quality monitoring is essential in order to evaluate the negative effects of these substances and to design the most efficient measures for a sustainable development.

Key Words: aerosol particulate matter, anions, cations, polycyclic aromatic hydrocarbons, dioxins

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O 34A – Trace element profiling of hair in the neonate as a possible marker of maturity

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Abstract

Purpose: Determination of the trace element profiling of the hair in the neonate according to gestational age.

Experimental description: Trace element profiling using energy dispersion X-ray fluorescence technique in a sample of 80 neonates divided in groups according to gestational age.

Results: The composition of the studied elements in the analysed hairs was very similar between groups; the biggest difference observed between the control and the samples is the amount of aluminium. It was also verified that along each hair the concentration of most remains the same, i.e. their composition is about the same from root to tip. Regarding the analysed elements, sulphur as the highest relative concentration, ranging from 86-90%, followed by chlorine with 5-7% and calcium with 1-3%. The relative concentration of the remained studied elements is below 1% each. Furthermore, as the gestational age increase from group to group, the values of aluminium, iron, copper and zinc decrease and those of sulphur and phosphorus increase. On the other hand, chlorine, calcium and silicon, don't present apparent tendency for different gestational ages.

In terms of the total amount of trace elements, it was recorded for full-term, late preterm, very preterm and extreme preterm, the respective values of 20100 ± 2200 , 15300 ± 1800 , 12700 ± 1500 and 9600 ± 1400 mg/kg. The verified differences have weak evidence of significance. This can be attributed to the low volume of the samples and to other factors that may also contribute to the absorption of nutrients by the fetus besides the gestational age.

Besides the differences verified between groups there was ~~also~~ a substantial gap between them and the values obtained for the standard and adult sample, respectively, 64200 ± 2700 and 49100 ± 2600 mg/kg. These differences are very likely due to, again, the low volume of the samples and the heterogeneity of the hairs themselves. Finally, it's interesting to note that in some of the samples it was possible to observe the presence of iodine, signalling, most likely, some type of contamination at the time of labour.

Conclusions: The goal of the study was reached, as it was possible to analyse and differentiate the concentration of trace elements in different gestational age groups. During the study it was noticed that the data obtained is somewhat dependent on the volume analysed since the studied hairs were on the same scale

as the focal spot of the spectrometer. As such, the obtained values are affected by a systematic uncertainty. One possible solution could be using tablets made out of the analysed samples. However, considering that the donors are neonates, most of which preterm, it's highly doubtful that there would be enough hair samples in each donor to make a tablet and/or that the parents would give permission to remove such a considerable amount of their children's hair.

Key words: hair, neonate, ultrastructure, trace element, X-ray fluorescence.

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O 35A – Effect of a water-based drilling waste on receiving soil properties and plants growth

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Abstract

One of the primary concerns of the rising growth of the petroleum industry in Alberta, Canada is on the proper management of drilling streams generated during drilling operations. Land spreading represents an attractive option for managing water-based drilling waste, however, the impact on soil properties and phytotoxicity remains largely unknown. This study was carried out to assess the relative effects of recommended guideline for land spraying loading rate application on soil properties and plants growth. The source of the drilling waste material was from an active well site drilling program. Composite representative samples of the drilling waste streams which also included the flocculated finer solids from the collection bins were transferred into a clean 20 L high density polyethylene pail. The pail was then homogenized and stored at 8 °C in a refrigerator prior to initiate the analyses. Soil sample used in this study was retrieved to a depth of 10 cm from a cultivated land located in Southern Alberta and represents soil type with physicochemical properties generally found in the area. The drilling waste was analyzed for dry Bulk Density, pH, EC, TDS, chloride, sodium, calcium, magnesium, SAR and COD. Maximum application rate for a regulated parameter was calculated according to the following equation: $MAR (m^3ha^{-1}) = P_{max} (kg ha^{-1}) \{ [1 \times 10^6 (mg kg^{-1}) / P_w (mg kg^{-1}) \times DBD (kg m^{-3})]$. The drilling waste loading rates were investigated for their phytotoxicity on Alfalfa (*Medicago sativa*), Oat (*Avena sativa*), Barley (*Hordeum vulgare*) Corn (*Zea mays*), and Radish (*Raphanus sativus*). Drilling was applied at 0 x, 10 x, 40x, and 50 x in excess of the recommended loading rate. Following weighing, 500 g of the treated soil samples were transferred into respective germination pots (15 cm ID x 12 cm), covered and appropriately labeled. Each pot was seeded with a bio-indicator and spatially optimized as recommended by the seed company. The experiment was carried out in triplicate. Plants growth was monitored for a period of ten days. Drilling waste applied at 10 times above recommended loading rate improved the growth and germination rate of all plants excluding radish. Loading rates in excess of 40 and 50 times had a deleterious effect on radish, corn and oat but not on alfalfa and barley. Germination rate decreased as waste loading rate increased. Effects on soil physical and chemical properties were more pronounced at the 40 and 50 times exceeding recommended loading rate. Significant changes in soil parameters occurred at the higher rates in terms of increase in soil porosity, pH, EC, hydraulic conductivity, SAR and textural classification. This study indicates that the applications of this type of

water based drill cutting if executed at an optimal loading rate, may improve soil quality and results in better plant growth.

Key Words: Drilling waste; Land spreading; Mud; Plant growth; Soil quality; Phytotoxicity

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O 36A – *Callitriche*: a brief story of unusual phytoremediation capabilities

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Abstract

Key words: aquatic environment, *Callitriche*, chromium, phytoremediation, thallium

The aim of the presentation is to review the extraordinary phytoremediation capabilities of *Callitriche cophocarpa*. This plant species is a higher aquatic plant (macrophyte), the most common representative of the *Callitriche* genus in Poland and elsewhere in Europe. It grows in stagnant as well as in running water. *C. cophocarpa* shoots are able to accumulate Cr(III) and Cr(VI) compounds extensively, and to purify waters from excessive concentrations of Tl, Cd, Zn, and Pb. The presented results deal with both physicochemical processes and the ones controlled by metabolism of the living plant. For the experiments a number of different analytical methods were applied (i.e. ICP-MS, L-band EPR, micro-XRF, scanning force microscopy, scanning electron microscopy with EDS detection, fluorescence and absorption spectrometry, sequential chemical extraction, environmental Microtox® toxicity test, modeling of adsorption isotherms).

It has been demonstrated that:

- 1) according to adsorption isotherms the maximum Cr accumulation reaches up to 5.1% of the plant dry mass in the case of Cr(III) and 1.8% in the case of Cr(VI);
- 2) plants are capable of removing Cr(III) ion from the solution with 100% efficiency;
- 3) Cr binds strongly with the plant tissue in a way that depends upon the oxidation state in which it occurs in solution; after incubation of the plants in solution with Cr(III), Cr binds very strongly in the form of chelate or organometallic complexes; after incubation in solution with Cr(VI), Cr can be remobilised easily as it occurs in the form loosely bound to the matrix;
- 4) *C. cophocarpa* conducts the intratissular reduction of the highly toxic form of Cr(VI), without the reduction of Cr(VI) in the solution; such a result indicates the lack of Cr phytostabilisation based on the release of reducing agents to the solution as it occurs in the case of some microorganisms;
- 5) Cr distribution in *C. cophocarpa* tissues depends on the speciation of the element: after incubation in solution with Cr(III) ions, Cr is accumulated in great quantities only in hairs/trichomes on the surface of leaves and stems; in plants exposed to Cr(VI), chromium is present also in vascular bundles, however, in much smaller quantities;

6) *Callitriche* reveals above-average abilities in phytoextraction of extremely toxic compounds of Tl and Cd, as well as Zn and Pb;

7) remediation of Tl, Cd, Zn, and Pb is based on the strong bioconcentration of these elements in tissues of the studied plant (BCFs often > 1000), with the simultaneous complete removal of the toxicity of the polluted water;

8) the photosynthetic apparatus of *C. cophocarpa* demonstrates high tolerance to pollution by the studied metallic compounds.

The obtained results can contribute to the development of knowledge pertaining to mechanisms controlling phytoremediation of metallic compounds in water systems. Sorption capacity found for dry biomass of *C. cophocarpa* is in the case of Cr(III) greater than other adsorbing agents, including activated carbon that were examined earlier by other authors and, in the case of Cr(VI) comparable to majority of chromate natural adsorbents. As the studied species is widely distributed in Poland and across the world, is a perennial one and shows relatively large biomass increments, the results of my research studies will also, I hope, translate into applied use in the very next future.

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O 37A – Chromate bioremediation mechanisms in prokaryotic and eukaryotic organisms

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Abstract

Although chromium occurs naturally in the lithosphere in a variety of mineral forms, the environmental threat caused by pollution with toxic compounds of this heavy metal has been increasing dramatically within recent years. This is mainly due to anthropogenic activities involving numerous industrial applications of Cr and extensive use of vehicular transport. Thus, decontamination actions need to be undertaken and bioremediation appears as a promising method to solve the problem.

Among many potential Cr oxidation states, the hexavalent, oxyanionic chromate form, CrO_4^{2-} , is generated predominately upon industrial activities and is the most hazardous one, detrimental to humans and other organisms. This is in contrast to other heavy metals that usually appear as cationic species and therefore Cr(VI) requires different pathways for its bioconversion. Chromate ion is a strong oxidant and tends to react with any organic molecules carrying oxidizable groups. It is relatively soluble and as a structural analog of phosphate and sulfate becomes actively transported inside cells across biological membranes *via* anion transporters. Then, upon reactions with cellular factors it undergoes reduction to the final trivalent oxidation state which is less toxic due to the reduced mobility and reactivity as well as the tendency to form insoluble complexes with various organic compounds. However, chromate bioreduction is in fact a gradual and complex activation route involving formation of Cr(V) and Cr(IV) intermediates that generate reactive oxygen species. This process is generally regarded as responsible for the oxidative cell damage resulting in genotoxic, mutagenic and carcinogenic action of Cr(VI).

The abundance of chromium compounds in the environment enabled to evolve numerous Cr-tolerant species that have developed diverse resistance mechanisms. Among these are pro- and eukaryotic microorganisms: bacteria, yeast, and microalgae as well as higher plants, all able to proliferate in the presence of Cr compounds. From the point of view of these organisms, chromate bioremediation may be considered as any attempt aimed at the reduction of the level of Cr(VI) toxicity. The experimental data collected to date and based on extensive research proves that there is no universal scheme for chromate detoxication and elevated tolerance. Various mechanisms identified in different organisms are presented and discussed; they include specific and non-specific, intra- and extra-cellular ones, passive biosorption and metabolically-driven processes (transport,

cellular uptake and chromate efflux), enzymatic and non-enzymatic bioreduction, complex formation, precipitation and biosequestration.

Some of the cellular bioremediation strategies may be adopted in efforts to cope with chromate environmental pollution with the use of Cr-tolerant, indigenous, highly specific and preadapted organisms. In biotechnological applications, plants and microorganisms capable of enhanced chromate uptake and hyperaccumulation as well as of Cr(VI) extensive reduction are of particular interest since they may bring possibilities for elaborating cheap, non-invasive and efficient industrial-scale methods for soil reclamation and water cleanup, employed using either the *in situ* or *ex situ* approaches.

O 38A – Biosurfactants as additives to increase PAH release from soils or sediment and enhance remediation processes

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Abstract

Purpose: The aim of this study was to evaluate if biosurfactants, which are surface active agents produced by a wide variety of microorganisms, can increase the release of lipophilic organic pollutants strongly sorbed to soils or sediment and can, when used as additives, enhance the efficiency of some remediation processes. Examples of their usefulness are shown on the electrokinetic (EK) remediation of polycyclic aromatic hydrocarbons (PAHs) from contaminated sediment and on the bioremediation by biodegradation of phenanthrene (PHE) from polluted soils.

Experimental description: The experimental EK setup consisted of a sediment chamber and two electrode compartments (applied voltage gradient: 1 V.cm⁻¹), with two pumps filling each electrode compartment with aqueous solutions containing biosurfactants. The sediment was provided by a French Norman harbor from dredging. For biodegradation time-course experiments, spiked microcosms were established, containing various field-contaminated soils collected in Northern France and spiked with PHE (300 mg.kg⁻¹). Half of them were spiked with a biosurfactant (300 mg.kg⁻¹). Used biosurfactants were a commercial rhamnolipid or two cyclic lipopeptides of our own production, obtained from *Pseudomonas fluorescens* PfA7B or DSS73 strains cultures. PAHs were extracted from soils or sediment by microwave assisted extraction and analysed by GC-MS.

Results: The mobilization of PAHs by biosurfactants from contaminated sediment was first investigated through the study of their sorption isotherms. Cyclolipopeptidic biosurfactants (amphisin and viscosin-like) were effective for 2-3 ring PAHs desorption from the more highly retentive fine particles (clays) and the organic matter of sediment. Thereafter, a cyclolipopeptide and a rhamnolipid were tested as additives in EK experiments, in order to decontaminate sediment, improving PAHs desorption and migration to electrode compartments. Promising results could be obtained using the biosurfactants combined to citric acid, associated to the application of a periodic voltage gradient. But the biosurfactant concentration should be high enough in the purging fluids to favor the formation of micelles in the pore fluid over their sorption onto sediment particles. A rhamnolipid and the viscosin-like cyclolipopeptide were also investigated as potential biostimulating agents for enhancing PHE bioavailability and improving its biodegradation in two dissimilar soils. It appeared that the rhamnolipid was more able to slightly accelerate the natural biodegradation of PHE

in only one of the soils. The effect of rhamnolipid was negligible on the soil characterized by a fast PHE dissipation and the presence of efficient degrading bacteria. In contrast, the impact of rhamnolipid was slightly positive on the soil characterized by a slower PHE dissipation (so a longer geosorbents/PHE contact time) and a large diversity of less efficient degrading bacteria.

Conclusions: Biosurfactants can be usefull to enhance remediation processes when they are used at sufficient concentrations to form micelles in solution and favor desorption of strongly sorbed and low bioavailable PAHs.

Key Words: Polycyclic aromatic hydrocarbons, soil pollution, electrokinetic remediation, bioremediation, biosurfactant

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O 39A – Parasite and Pollutant: Toward Safe drinking water in Southeast Asia

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Abstract

Purpose: This study aimed to determine the current distribution of waterborne protozoan parasites and its association with physico-chemical parameters in various types of water samples from the four selected Southeast Asian countries, namely Malaysia, Philippines, Thailand and Vietnam.

Experimental description: A total of 221 water samples, 10 liters each were collected during April-October 2013 from Malaysia (53), Philippines (33), Thailand (120) and Vietnam (15). Ten liters of water sample each was processed to detect *Cryptosporidium parvum* and *Giardia lamblia* using an IMS method prior to enumeration via fluorescence microscope and qPCR analysis. Physico-chemical analysis indicated positive correlation of ammonia, nitrite, and nitrate with the number of (oo)cysts.

Results: Microscopically, all treated water samples from Malaysia, Thailand, and Vietnam were found negative for (oo)cysts, except from Philippines that were positive for *Cryptosporidium* (0.06 ± 0.19 oocysts/L) and *Giardia* (0.02 ± 0.06 cyst/L). Untreated samples were contaminated with *Giardia* (1.68 ± 8.18 cyst/L), 6 times higher compared to *Cryptosporidium* (0.28 ± 0.84 oocyst/L). This study is our first attempt to detect waterborne protozoan parasites in Southeast Asia via real-time PCR by targeting the 138-bp fragment for *C. parvum* and small sub-unit gene for *G. lamblia*, with detection limit of 0.2 (oo)cysts/L. The highest occurrence of *Giardia* was reported in the Philippines (55%), followed by Malaysia (23%), and Thailand (18%). All physical parameters and chlorine showed negative relationships for number of (oo)cysts/L and nitrate also

demonstrated a negative relationship with *Giardia* cysts/L. Meanwhile, other chemical parameters revealed a positive relationship with both of the waterborne protozoan parasites. The relationship between *Cryptosporidium* oocysts/L and nitrite showed a moderate positive correlation with r-value equals to 0.7045.

Conclusions: The presence of *Cryptosporidium* and *Giardia* in both raw and treated water samples explained the potential risks of zoonotic transmission. Physico-chemical parameters can be used as baseline to indicate the contamination of waste products in the water, in order to correlate with the presence of (oo)cysts. Further study is recommended particularly in introducing heavy metals analysis to provide more extensive platform for risk assessment with the occurrence of waterborne parasites contamination in this region.

Keywords: *Cryptosporidium parvum*, *Giardia lamblia*, Physico-chemical, Microscopy, Real-Time PCR and Southeast Asia

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O 40A – Multi-functioned remediation technique for inorganic pollutants in soil, using a nano-sized calcium dispersing system

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Abstract

Japan is beset with environmental problems created by naturally-occurring (*e.g.* volcanic) or anthropogenic heavy metals like cadmium (Cd), arsenic (As), and lead (Pb) *etc.* (*e.g.* huge governmental projects such as tunnel constructions for Shin-kansen bullet train). Therefore, many chemists had focused their research on the development of separation and solidification techniques for heavy metals (HMs) in polluted soils. In numerous cases, such techniques depended on the difference of specific gravity between pollutants and soil particles, taking into account soils' moisture contents. However, the presence of water is often considered as a disadvantage in HMs direct immobilization in soils. We have recently shown that nano-size metallic calcium/calcium oxide (nCa) and/or iron dispersing (Fe-nCa) mixtures are most effective for HMs immobilization and volume reduction method under dry condition. Simple grinding achieved trapping of 85-90 wt% of HMs, but the value can be enhanced further to 98-100 wt% by using additional nCa. Moreover, due to the magnetic behavior of the soil treated with the Fe-nCa system, two soil fractions can be easily separated: 36-45 wt% of magnetic soil (with 85-95 % HMs concentration) and 64-55 wt% of nonmagnetic soil fraction (presenting a much lower HMs concentration – only 10-20 %). Fe-nCa treatment reduced the leaching concentrations of HMs to values lower than the Japan soil elution standard. regulatory threshold of 0.01 mg/L for As, Cd, and Pb; and 0.05 mg/L for Cr.

Moreover, the method was effective in treating genuine radioactive cesium contaminated soils (contamination that occurred subsequent to the Fukushima Dai-ichi nuclear power plant major accident, in March 2011). Simple stirring of the contaminated soil with the Fe-nCa system achieved about above 90 % of radioactive Cs decontamination, along with a volume reduction level of *ca.* 50-60 %. In this study, we demonstrated the effectiveness of the Fe-nCa method for the rapid remediation of real radioactive cesium contaminated soils, under dry conditions, and the challenges posed by devising an effective soil-treating machine.

Key Words: cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), radioactive cesium (Cs), nano-size metallic calcium, immobilization

Acknowledgements: The authors gratefully acknowledge financial support for this study from a Grant-in-Aid for Scientific Research (B) [KAKENHI: 15H02844] from the Japan Society for the Promotion of Science (JSPS), and Special thanks to TODA KOGYO Corp.

O 41A – Detection of toxic Pb²⁺ and Hg²⁺ ions using fluorescent chemosensors and functionalized nanomaterials.

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Abstract

Purpose: In the last decade, the synthetic chemistry and applied nanomaterials for toxic metal ions detection have been dominated by the development of more selective, sensitive and inexpensive systems. Metal ions play a significant role in living systems, but when in excess they have a very negative toxic impact in the environment. The chronic and severe exposure to heavy metal ions, such as Pb²⁺ and Hg²⁺ produce a substantial impact on human health being the leading cause of human diseases as cancer and cardiovascular disorders. It is estimated 143 000 deaths/year due to human exposure to lead. Herein, an outlook of several synthetic probes from ultraviolet to far-red visible excitable chromophores for colorimetric and fluorimetric detection of Pb²⁺ and Hg²⁺ metal ions are discussed, as well as, their functionalization into nanomaterials surface to achieved lowest detection limits and in solid supported devices.

Experimental description: Sensorial ability of compounds derivatives from benzoxazole, coumarin, fluorescein and porphyrin chromophores were studied towards toxic Pb²⁺ and Hg²⁺ metal ions. Interaction studies were carried out in solution (organic or aqueous) and in solid supported devices. These studies were monitored by absorption and emission spectroscopy.

Results: Colorimetric changes were observed upon addition of Pb²⁺ and Hg²⁺ metal ions. In all cases a CHEQ effect was observed with the addition of mercury (II) metal ion. Metallic and silica nanoparticles functionalized with these compounds led to a decrease of the detection limit.

Conclusions: The sensorial ability to Pb²⁺ and Hg²⁺ of probes with visible excitable chromophores was successful evaluated in solution and in solid supported devices allowing the detection of fewest amounts of these metal ions.

Key Words: Colorimetric, Fluorimetric, Chemosensors, Lead(II), Mercury (II)

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O 42A - Assessment of prenatal exposure to DDT and DDE of a Bolivian population cohort

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Abstract

Purpose: The main aims of the present study were to evaluate the association between prenatal concentrations of o,p'-DDT, p,p'-DDE, and the exposure of the mothers in a cohort study and to examine association between the concentrations of o,p'-DDT, p,p'-DDE and the neonatal TSH levels.

Experimental description: From January to March 2013, 242 eligible mother-son pair registered at the Percy Boland Hospital were recruited and enrolled at delivery. Exclusion criteria were: maternal presence of serious chronic disease, such as diabetes, hypertension, or thyroid disease; pregnancy complication that could affect growth or development. Prenatal concentrations of o,p'-DDT and p,p'-DDE were determined in cord blood. Samples of cord blood were collected and immediately coded; the serum was separated and stored at -40°C until chemical analysis. The samples were analyzed by gas chromatography/mass spectrometry. TSH was measured in a cord blood sample spotted on a filter paper, which was routinely obtained shortly after birth in the hospital. Data on potential predictors of DDT/DDE concentrations were gathered by questionnaire and multivariate analyses of the results were performed.

Results: DDT was detected in 11.6% of the population and DDE was detected in 55% of the subjects. Geometric mean concentrations of o,p'-DDT and p,p'-DDE were 123,19 and 311,64 ng/g lipid. Geometric mean of neonatal TSH was 2.092 mU/L. In the multivariate models, the predictors of DDT/DDE concentrations included mother's age, body mass index (BMI) at the beginning of pregnancy, increase of weight during pregnancy, parity, gestational age, educational level, place of residence and diet. The neonatal TSH levels didn't show statistically significant correlation with DDT/DDE concentrations; however, they showed a negative trend. Negative quadratic association between DDT concentrations and ponderal index was found.

Conclusions: The study population showed high concentrations of DDT/DDE in cord blood, that are likely to be caused by a contaminated local environment due to the intense historical use of pesticides in the region.

Key Words: Persistent organic pollutant, DDT, DDE, prenatal exposure.

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O 43A – Accumulation and recovery capacity of heavy metals in sand mine ponds of the Otamiri River in Owerri, Nigeria

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Abstract

This study investigated the levels, index of accumulation and recovery capacity of heavy metals (Pb, Cd, Cu, Ni, Zn, Fe, Mn) in sand mine ponds of the Otamiri River in Owerri, Nigeria during the wet season of 2012. Water (WC) and sediment samples (SD) were collected from six sampling points, with WC 1-WC 3 and SD 1-SD 3 located within a derelict mine pond and WC 4-WC 6 and SD 4-SD 6 located within an actively mined pond. The pH was determined *in situ* and levels of heavy metals measured with the atomic absorption spectrophotometer. The student's t-test, index of geoaccumulation (Igeo), accumulation factor (AF) and pond recovery capacity (PRC) were computed for the ponds. There was significant spatial heterogeneity in mean levels of the heavy metals in sediments ($t=0.029$) at $P<0.05$, with higher levels of metals also recorded in sediments than water columns. The order of Igeo was $\text{Fe (5.959)} > \text{Zn (4.932)} > \text{Cu (4.743)} > \text{Mn (4.326)} > \text{Pb (3.214)} > \text{Ni (2.483)} > \text{Cd (1.649)}$, AF was $\text{Zn (1.513)} > \text{Cd (1.179)} > \text{Fe (1.082)} > \text{Ni (1.048)} > \text{Mn (1.042)} > \text{Cu (1.032)} > \text{Pb (0.987)}$ and PRC was $\text{Zn (33.891)} > \text{Cd (15.165)} > \text{Fe (7.604)} > \text{Ni (4.608)} > \text{Mn (4.047)} > \text{Cu (3.052)} > \text{Pb (-1.373)}$. Active mining led to extreme contamination of the ponds with Fe, strong to extreme contaminations with Cu, Zn and Mn, strong contamination with Pb, moderate to strong contamination with Ni and moderate contamination with Cd. However, Pb showed deficit recovery capacity and this could portend unfavourable ecological consequences on resident biota and raises public health concerns among resource dependants of the river. Strict enforcement of regulations on in-stream sand mining should be applied.

Keywords: in-stream sand mining, geoaccumulation index, pond recovery capacity, sediments.

O 1B – Cellular imaging of cadmium in resin sections of arbuscular mycorrhizas using synchrotron micro X-ray fluorescence

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Abstract

Purpose: Arbuscular mycorrhizal (AM) fungi function as extended roots and take an active part in plant acquisition of nutrients and also soil pollutants, such as heavy metals. To know how mycorrhizal fungi play roles in cadmium (Cd) accumulation in roots, a histological approach is essential to analyze elemental flow, because host and fungal cells are integrated in the endosymbiotic tissues. An objective of this study is to establish a method to observe localization of Cd-K α at subcellular levels using X-ray fluorescence (XRF) imaging with a synchrotron irradiation microbeam in resin embedded sections of mycorrhizas.

Experimental description: Extraradical hyphae and mycorrhizal roots of *Lotus japonicus* - *Rhizophagus irregularis* (LjRi) and *Allium cepa* - *Gigaspora margarita* were prepared for resin embedding by either immersion of tissues in liquid propane (PF) or high pressure freezing (HPF), followed by a freeze-substitution. On the thick sections, XRF imaging by a synchrotron radiation microbeam was conducted at SPring-8. To evaluate the methodology, distributions of Cd in HPF mycorrhizal roots were compared between two treatments; Cd was exposed either to both the roots and the extraradical hyphae, or to the extraradical hyphae only. Sections of extraradical hyphae of *G. margarita* exposed to Cd were also examined by elemental mapping of by electron dispersive X-ray spectrometry, and then stained for polyphosphate (polyP).

Results: In HPF LjRi mycorrhizal roots grown in a Cd contaminated soil, Cd was detected in the host cell wall and the fungal structures; however, if Cd was added only to the extraradical hyphae, the element was observed only in the intraradical fungal structures. A positive correlation between distributions of Cd and P was revealed in the vacuole of extraradical mycelium of *G. margarita*, which suggested Cd as a counter ion of polyP.

Conclusions: These results suggested that there was no Cd relocation in rapidly frozen resin embedded materials and usefulness of this methodology.

Key Words: *Gigaspora margarita*, *Rhizophagus irregularis*, polyphosphate, synchrotron micro XRF, EDS-SEM

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O 2B - How to improve toxicological expertise of environmental compartments?

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Abstract

Environmental pollution has become a serious problem of the current century and is definitely caused by human activity. Because of this many approaches are used to assess the quality of environmental compartments. One of them are toxicological studies focused on evaluation of toxic effects of chemical substances on living organisms. Environmental toxicology involves the studying of harmful sources, their impact, transformations, and effects of both natural and synthetic chemical compounds in the environment. One of the current trend in environmental toxicology is an application of microbial tests mainly because of the similarity of complex, biochemical functions with higher organisms. However, in many cases microbial tests deliver only general information concerning the toxicity of the sample identifying positive or negative effect or giving an answer in the form of toxicological metrics as EC₅₀, LD₅₀, etc. Due to the fact that simple confirmation or negation of toxic effects in many cases is not sufficient an application of sophisticated data treatment methods which handle both physiochemical, analytical, geographical and toxicological data become desired.

The topic of the study concerns an application of cluster analysis, principal component analysis, self-organizing maps and other methods as tools used in supporting of toxicological expertise of environmental compartments. The comprehensive assessment of usability of mentioned method in environmental toxicology was done and presented in the form of several case studies.

Key Words: Microtox®, Spirotox, cluster analysis, self-organizing Kohonen maps, principal component analysis, data mining

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O 3B – Evaluation of toxicity of mixtures of TCS, SLS and zinc by the use of Microtox® and Spirotox tests

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Abstract

Purpose: An annual production of new chemical compounds reaches 2 thousands compounds, while humans use 60 thousands of various organic compounds every day. Majority of them enter to the environment and our body due to the use of cosmetics, cleaning products and processed food. Because environmental toxins frequently exhibit a synergistic effect we examined the toxicity of both single compounds (triclosan (TCS), sodium lauryl sulfate (SLS) and Zn^{2+}) as well as their mixtures. All substances are commonly added to everyday products. TCS is a synthetic, broad-spectrum antimicrobial agent. SLS is an organic chemical compound which is extensively used as ionic detergent, while Zn^{2+} is commonly used as an ingredient of medicines.

Experimental description: Evaluation of toxicity of mixtures of TCS, SLS and zinc was accomplished by the use of Microtox® and Spirotox tests. In case of Microtox® system toxicity is the function of inhibition of *Vibrio fischeri* bacteria bioluminescence, while Spirotox is a short-term acute toxicity test with a large ciliated protozoan *Spirostomum ambiguum*. In the first stage of the experiments 50% of effective concentration (EC₅₀) was determined. Subsequently, the toxicity of twelve different mixtures of TCS, SLD and Zn^{2+} was evaluated in order to determine their antagonistic or synergistic effects.

Results: In Microtox® test EC₅₀ ranged between 22 and 84.5% after 15 minutes and between 18 and 48.5% after 30 minutes. The lowest toxicity was determined for mixture of TCS and Zn^{2+} . Generally, in case of those two-ingredient mixture toxicity was correlated with concentration of TCS. A mixtures of TCS and SLS were characterized by higher toxicity. Similarly as before, in this case, an increase in the concentration of triclosan in the mixture caused an increase of toxicity. The highest toxicity was found for three-ingredient mixtures. Constant concentration of TCS, increasing concentration of SLS and decreasing concentration of Zn^{2+} cause an general effect in the form of increasing toxicity. The effect was measurable after 15 minutes.

Protozoa behaved differently in the studied mixtures. An increase concentration of the test substances in the mixture caused an increase in toxicity. The most toxic mixtures were two-ingredient mixtures of TCS and SLS, while three-ingredient mixes were not characterized by a higher toxicity.

Conclusions: Test organisms differ in their susceptibility to various classes of chemical agents. Triclosan and SLS were more toxic to bacteria while zinc was more toxic to protozoa.

Key Words: triclosan, sodium lauryl sulfate, toxicity, EC_{50} , *Vibrio fischeri*, *Spirostomum ambiguum*

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O 4B - Chemical, thermal and physical modification of water treatment residuals and their use as an As(III) and As(V) sorbent

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Abstract

Recently, much attention has been devoted to the use of industrial wastes containing iron and/or aluminium oxides as As(III) and As(V) sorbents. Such wastes exhibit high adsorption capacity toward arsenic and heavy metals, but their physical form (small-particle sludge) makes their utilization quite difficult. The aim of this research was to study the adsorptive properties of water treatment residuals (WTRs) (from deironing and demanganization processes) towards As(III) and As(V), as well as the modification of their sorptive properties and the physical form.

The raw material (WTRs) was dried at 25°C for 72 h and then ground. Chemical treatment of WTRs consisted of washing of dried WTRs in HCl solution (0.05 M; 0.1 M; 0.4 M; 1 M) or 3% H₂O₂ for 25 min, rinsing with demineralized water and drying. The thermal processing consisted of heating of dried WTRs for 6 h at 100, 300, 500 and 700°C. The modification of the physical form of WTRs was conducted by its entrapment in calcium alginate beads. It was done by dropping WTRs, dispersed in sodium alginate solution (1-3%), into CaCl₂ solution. The sorptive characteristics of raw and modified WTRs towards As(III) and As(V) were determined by conducting kinetic and equilibrium studies. The obtained results were analyzed using kinetic reaction adsorption models or isotherm models. The raw and/or modified WTRs were characterized by X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR) and a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometry microanalyzer (EDS). Specific surface area and the porous characteristics of the hybrid polymer were determined from the adsorption isotherms for liquid nitrogen at 77 K using an Accelerated Surface Area and Porosimetry Analyzer.

The raw WTRs exhibited excellent sorptive properties towards both forms of arsenic, and the determined maximum sorption capacities were 132.2 mg As(III)/dm³ and 76.7 mg As(V)/dm³ (at neutral pH). The better results obtained for As(III) can be explained by the manganese(IV) oxide content in WTRs. As(III), in the presence of MnO₂, undergoes oxidation to As(V), which leads to the reductive dissolution of manganese oxide, resulting in the release of Mn²⁺ ions, which are adsorbed on the surface of the sorbent, giving it a positive charge and, in consequence, facilitating the adsorption of the formed arsenates. It also caused that As(III) adsorption was less pH dependent. Before entrapping WTRs in alginate beads, the raw material was modified chemically and thermally, in order to further improve its sorptive properties. The best results were obtained by washing WTRs with 0.05 M HCl, which increased the adsorption efficiency up to 7%. In contrast, the influence of thermal treatment was negative and caused a significant decrease in adsorption efficiency. Entrapping modified WTRs

in alginate gel allowed us to obtain stable, spherical beads (2.5 mm diameter) containing an inorganic deposit. In order to obtain sorbent with optimal properties, various parameters were investigated, e.g. concentration of sodium alginate solutions (1-3%), the amount of entrapped WTRs (1-5%), and the diameter of the gel beads. The obtained product, apart from good adsorptive properties towards As(III) and As(V), exhibits excellent hydraulic properties allowing its use in column processes, most desired from the technological stand-point.

Key Words: Adsorption, iron oxides, arsenic, water treatment residuals, hybrid polymers, alginate

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O 5B – Study of environmental criteria of heavy metal Cr(VI), Pb and Cd in China

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Abstract

Purpose: Development of aquatic life criteria and soil environmental criteria for Cr(VI), Pb and Cd in China using the toxicity data of native species.

Experimental description: First of all, toxicity data of native species for Cr(VI), Pb and Cd were selected. The quality and quantity of selected toxicity data were checked. Secondly, acute/chronic toxicity tests were carried out when toxicity data of native species were lacking. Thirdly, aquatic life criteria and soil environmental criteria based on toxicity data of native species were derived using the species sensitivity distribution method.

Results: The acute/chronic toxicity data of aquatic life for Cr(VI), Pb and Cd were selected. The chronic toxicity of terrestrial species for Cr(VI), Pb were tested. The aquatic life criteria based on toxicity data of native species for Cr(VI), Pb and Cd were derived using US-SSD method. The soil environmental criteria based on tested toxicity data for Cr(VI), Pb were derived using the log-logistic SSD method.

Conclusions: The criteria maximum concentrations of aquatic life for Cr(VI), Pb and Cd were 17.73, 131 and 1.15 µg/L, respectively. The criteria continuous concentrations of aquatic life for Cr(VI), Pb and Cd were 12.15, 5.1 and 0.12 µg/L, respectively. The soil environmental criteria for Cr(VI) and Pb were 1.5~7.7 and 31.7~158.3 mg/kg, respectively.

Key Words: environmental criteria, aquatic life criteria, soil environmental criteria, native species, Cr(VI), Pb, Cd, species sensitivity distribution

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O 6B - How CO interacts with metal cations exchanged zeolite: a theoretical investigation

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Abstract

Carbon oxides are involved in many chemical and industrial processes and their removal is of great importance to reduce detrimental environmental and climate impacts. Zeolites are generally classified among the most efficient porous materials for physisorption based applications industrially used for the selective adsorption of gases. Single and multiple adsorption of CO in zeolite faujasites containing metal cations were investigated through DFT quantum chemical calculations. DFT calculations were chosen to investigate and predict the adsorption energies, the geometries of the structures of the metal sites upon CO adsorption and the IR CO stretching signal of CO interacting with copper or alkalis exchanged faujasite zeolites.

Periodic structures were optimized using the VASP program and the PBE exchange-correlation functional. They were also optimized using the Crystal program and employing the B3LYP hybrid functional with Grimme dispersion corrections to account for long range energy interactions. For each model, all the atoms were allowed to relax.

Adsorption of CO in faujasite type aluminosilicate zeolite occurs in the largest cages and mainly on cations. Different distributions of the extra-framework cations in the faujasites can be obtained by changing the Si/Al ratio. Faujasite zeolites allow controlling in a large range the Si/Al ratio and to compare Si rich faujasite (large Si/Al ratio) to Al rich faujasite (Si/Al=1).

We showed how the initial position of the cations in the zeolite framework may change upon addition of CO and depends on the nature of the cation, being copper or alkali (K, Na and Li)[1-3]. Using Grand Canonical Monte Carlo simulations, the calculated isotherms provide a clear picture of the adsorption of CO on Na faujasites depending on the CO pressure and Si/Al ratio. [4] In the present study we compare the adsorption and coordination of CO on Na cations and Cu cations and predict the enthalpy values of adsorption. Theoretical calculations provide reliable energetic and spectroscopic (vibrational) properties. Both the formation of single and multiple CO adsorptions on sodium cation-exchanged faujasite using DFT approaches were investigated.

Theoretical investigations of CO adsorption in metal cation exchanged faujasite provide a detailed description of the structure and lead to valuable insights about the coordination of metals with the zeolite material and with CO

and about the nature of the interactions. Because such theoretical strategy is very efficient it can be applied to determine the affinity of pollutants with metals in materials and biomolecules.

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Key Words: zeolites, faujasites, adsorption, CO, metals, DFT, periodic, enthalpies, vibrations, isotherms

O 7B - Calcium signaling and the response to heavy metal stress in *Saccharomyces cerevisiae* cells

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Abstract

Purpose: Heavy metal pollution represents a threat to water supplies, agriculture soils, human and animal health. Heavy metals are challenging pollutants as they are natural components of the earth's crust, they are persistent in the environment and they are non-degradable. The immediate response to pollutants is essential for cell survival being often transduced by Ca^{2+} ions, which are used as second messenger by virtually all eukaryotic cells. To understand the ways in which cells sense the presence of toxic concentrations of metals, the involvement of Ca^{2+} in the response to high Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , or Hg^{2+} was investigated in *Saccharomyces cerevisiae* cells.

Experimental description: To see if the cell response to excess Me^{2+} was mediated by Ca^{2+} , the modifications in cytosolic Ca^{2+} were recorded using the Ca^{2+} -dependent photoprotein, aequorin. Involvement of Ca^{2+} channels and exchangers in Me^{2+} tolerance was investigated, along with the Ca^{2+} signaling profiles of yeast cells with defects in Me^{2+} cellular transport.

Results: The yeast cells responded through sharp increase in cytosolic Ca^{2+} when exposed to high Cd^{2+} , and to a lesser extent to Cu^{2+} , but *not* to Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , or Hg^{2+} . The cell exposure to high Cu^{2+} determined broad and prolonged Ca^{2+} waves into the cytosol which showed a different pattern from the Ca^{2+} pulses induced by high Cd^{2+} . The mechanisms of Ca^{2+} -dependent response to surplus Cd^{2+} and Cu^{2+} are discussed.

Conclusions: The tolerance to high Cd^{2+} often correlated with sharp Cd^{2+} -induced cytosolic Ca^{2+} pulses, while the Cd^{2+} sensitivity was accompanied by the incapacity to rapidly restore the low cytosolic Ca^{2+} . On the other hand, the Ca^{2+} -mediated response to surplus Cu^{2+} depended on the cell possibility to restrict the reduction to- and the accumulation of Cu^{+} .

Key Words: heavy metal stress, calcium signaling, aequorin, *Saccharomyces cerevisiae*

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O 8B – Analysis of polycyclic aromatic hydrocarbons (PAHs) in edible oils by capillary electrophoresis

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Abstract

Purpose: development of fast, selective, and sensitive methods involving capillary electrophoresis and laser-induced fluorescence detection for the determination of PAHs in food and environmental samples

Experimental description: Cyclodextrin(CD)-modified capillary electrophoresis is one of the most successful strategy for PAH separation. Classical bare silica capillaries 50 μm id x 49 cm (33.5 cm to detection window) were used. Separation buffers (background electrolytes) composed of a mixture of a neutral (methyl- β -CD) and an anionic CD (sulfobutyl ether- β -CD) were involved. A few percent of methanol were also added to the background electrolytes for improvement of PAH solubility, but also for separation selectivity. Indeed, the separation mechanism is based on the differential distribution of PAHs between the background electrolyte, the neutral CD, traveling with the electroosmotic flow, and the negatively charged CD, traveling slower than the electroosmotic flow. The differential distribution is linked to both PAH hydrophobicity and shape, leading to high selectivity. For selective and sensitive detection, a laser induced-fluorescence detector ($\lambda_{\text{exc}} = 325 \text{ nm}$) was implemented.

Results: Two new CD-modified capillary zone electrophoresis separation methods were first optimized using experimental design strategies for the separation of (i) the 8 PAHs common to the two priority lists (US-EPA and EFSA) and (ii) the 19 PAHs which fluoresce at 325 nm and are targeted by both agencies. These optimization approaches were based on a central composite design composed of 3 factors: the concentrations of the anionic sulfobutyl ether- β -CD and the neutral methyl- β -CD, and the percentage of methanol in the background electrolyte. Using a desirability analysis, a rapid screening method allowed separating the 8 priority PAHs in less than 10 min, whereas the other method enabled to simultaneously separate the 19 PAHs in 15 min. For the first time, these CE separation methods were successfully used for the determination of PAHs in edible oil extracts, proving their suitability for real world sample analysis.

Conclusions: New fast and sensitive methods for the determination of PAHs in food and environment were developed. Thanks to designs of experiments and an original computational approach, full resolution of either

8 priority PAHs or 19 PAHs was reached. Applications to real edible oil sample extracts were successfully carried out.

Key Words: polycyclic aromatic hydrocarbons, edible oils, capillary electrophoresis

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O 9B – Analysis of phytochelatins in plants stressed with mercury: some real examples

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Abstract

Mercury is a global pollutant that together with its compounds constitutes one of the most toxic substances found in all environment compartments. It is well known that the incorporation of heavy metals into the cells of plants or animals can induce some mechanisms leading to modulate the possible harmful effects. One of these mechanisms is the synthesis of several compounds such as metallothioneins (MT), in the case of mammals and some fungi, or phytochelatins (PC_n), in the case of plants and algae. These substances are thiol-rich peptides which interact very efficiently with heavy metal ions minimizing the stress that these could provoke in living organisms. The capability of plants and algae to synthesize this kind of molecules has been used to remove heavy metals from contaminated soils or aquatic systems through a methodology named phytoremediation. The general structure of this set of peptides is (γ-Glu-Cys)_n-Gly (n = 2 to 5). Glutathione serves as the substrate of PC biosynthesis through the transpeptidation of the γ-Glu-Cys moiety of GSH onto a second GSH to form PC₂ or onto a PC_n molecule to produce an n+1 oligomer. For these reasons, the study of PC content in plants is highly relevant, as PCs could be used as indicators of metal pollution. In the present work some examples of plants subjected to metallic stress have been considered. The first one corresponds to the study of *Hordeum vulgare* plants that have grown in the presence of Hg(II) or in the simultaneous presence of Hg(II) and Cd(II); in the second example, a comparative study of the effects of different heavy metals is done; and finally, plants from the Almadén mining district have been considered. This zone is known for the largest deposits of mercury in the world yet discovered.

Several methodologies have been developed to analyze phytochelatins and related peptides. Among them, mass spectrometry is the most widely used technique, although other possibilities can be considered. In the research group we have developed a new analytical methodology that combines HPLC with electrochemical detection in a glassy carbon electrode as a sensible and cheap technique. With this methodology not only several PCs and related peptides can be separated and detected but also their mercury complexes.

Studies of *Hordeum vulgare* plants grown in the laboratory in conditions of Hg(II) stress show a clear growth inhibition when mercury is present in the medium. The content of PCs and their mercury complexes in shoots and roots indicated that in general concentration of thiols is higher in roots than in shoots and their concentration increased according to the amount of metal applied. The most abundant thiols in shoots were glutathione and its Hg complex, while in roots PC₂ and its complex had higher values, letting us to consider PC₂ as a marker of metal stress in this plant. If the induction of PC_n by Hg(II), Cd(II) and As(III) in *Hordeum vulgare*

plants is compared, an increase of PC_n content according to the heavy metal concentration supplied to the plant is observed in all cases. By other hand, the length of the PC_n chain depends on the level of metal concentration as well as on the metal supplied, and Cd(II) demonstrates to be the most potent inductor of PC_n.

Taking into account studies of plants (*Asparagus acutifolius*) collected in the Almadén mining district, it is interesting to point out that although it is one of the most Hg-contaminated places on Earth, only a 0.33% of the total content of mercury is organic mercury and only a 1.94% is extracted with EDTA. Studies done in this area show a clear correlation between total thiol groups and concentration of Hg in plant tissues and soils. The findings of these studies highlight the important role of thiol compounds and their metal complexes in capturing and fixing Hg from soils, giving plants the capacity to deal with the heavy metal toxicity of polluted soils.

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O 10B - Alternative solvents to promote more sustainable analytical methodologies

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Abstract

Purpose: This presentation will discuss the applicability of a variety of solvents toward more sustainable analytical methodologies.

Experimental description: Analytical methodologies commonly make use of non-negligible volumes of volatile organic solvents (VOCs). VOCs are mainly employed in sample preparation and chromatographic separations, contributing to the generation of significant amounts of wastes. In this sense, the efforts made to fulfill the principles of green analytical chemistry have been mostly directed to the miniaturization of analytical systems. The development of alternatives to conventional VOCs, including bio-based molecular solvents, eutectic mixtures and ionic liquids, offers novel possibilities for greening analytical methodologies.

Results: The development of less harmful solvents is of paramount importance toward more sustainable chemical processes, and this is particularly important in the field of analytical chemistry. Challenges and opportunities that can arise in the implementation of alternative solvents in analytical methodologies are considered in this work.

Conclusions: This work shows the huge possibilities that novel solvents provide to the development of greener analytical methodologies. Particularly, the replacement of conventional solvents derived from fossil resources by solvents derived from natural and/or renewable resources is expected to significantly contribute to the decrease on the environmental, health and safety aspects of conventional analytical methodologies.

Key Words: green solvents; bio-based solvents; ionic liquids; deep eutectic solvents; method development

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O 11B – H₂O and CH₄ interaction with the stoichiometric and reduced CeO₂ (111) surface: a first-principles investigation

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Abstract

Purpose: By means of a first principle investigation, we propose the analysis of the interaction of water molecule and methane with the stoichiometric and reduced CeO₂

Experimental description: We use a theoretical-computational Density Functional Theory approach, within the ab-initio atomistic thermodynamic framework

Results: phase diagrams of the adsorbate–surface system under realistic environmental conditions is constructed and relevant transition phases are analyzed in detail, showing:

- 1 Water adsorption/desorption on the stoichiometric surface and oxygen vacancy formation in the presence of water vapor
- 2 A study of the vibrational contribution to the free energy to estimate the effect of this term on the stability range of adsorbed water
- 3 The conditions where partial oxidation of methane can occur.

Conclusions: This work brings an insight, from a first principle prospective, to the realistic condition to have partial oxidation of methane

Key Words: Cerium Oxide, Catalysis, Density Functional Theory

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O 12B - Abatement of industrial pollutants via the liquid phase wet air oxidation process (CWAO) using novel effective *nanostructured* oxide catalysts

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Abstract

Purpose: Huge water consumptions and continuous releases of pollutants in the environment by many industrial facilities urge effective industrial water decontamination technologies to enable an extensive recycle of process and wastewaters. The liquid phase heterogeneous catalytic oxidation with air (CWAO) offers a viable solution to the large-scale depollution of industrial effluents highly concentrated ($\text{COD} > 10 \text{ g/l}$) in substances refractory or toxic to biological treatment systems. Capitalizing on the advances during a 10 years research activity leading to a patent application for the synthesis of *nanostructured* MnCeO_x catalysts with improved adsorption and redox properties, this work is aimed at offering an outline of experimental data documenting the adequacy of the CWAO process for decontamination of industrial wastewaters.

Results: The preliminary achievement of this research activity allowed to ascertain the occurrence of a typical L-H reaction path explaining at once activity, selectivity and deactivation pattern of heterogeneous CWAO catalysts. Indeed, while the water decontamination efficiency depends on the removal of polluting compounds by surface adsorption, the further oxidation of adsorbed species is the rate limiting step also responsible of deactivation by carbonaceous deposits (*fouling*). Then, the development of a synthesis route strongly improving textural and redox properties allows to obtain *nanostructured* MnCeO_x catalysts with a superior performance in the CWAO of phenol in terms of water purification rate, phenol retention capacity, mineralization rate and resistance to deactivation by fouling. In addition, Table 1 compares the CWAO behavior of the developed catalysts toward some common industrial pollutants in terms of substrate and TOC conversion.

Table 1. Activity data of the MnCeO_x catalyst in the CWAO of various substrates at 150°C (P_{O_2} , 0.9 MPa; P_{tot} , 1.4 MPa).

Substrate	$X_{\text{sub}} (\%) - t (\text{h})$	$X_{\text{TOC}} (\%) - t (\text{h})$	$S_{\text{CO}_2^a}$
Phenol	100 - 0.15	97 - 6	91
p-cumaric acid	100 - 0.15	100 - 6	61
Acetic acid	100 - 6.0	97 - 6	71

a) CO₂ selectivity (e.g., extent of TOC mineralization) after 6h.

Conclusions: The good CWAO functionality of the MnCeO_x catalyst is further documented by a series of data on the purification of “real” wastewater samples coming from oil-mills, refinery, winery and detergent industries.

Key Words: Industrial wastewater; detoxification treatment; catalytic wet air oxidation (CWAO).

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O 13B – Development of molecularly imprinted membranes able to selectively recognize toxic organic compounds

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Abstract

Aim of this work was the development of molecularly imprinted membranes (MIMs) for the selective recognition of dimethoate, which is a pesticide used in agricultural productivity. It was identified as one type of organophosphorus pesticides listed in guidelines for drinking water by World Health Organization [1]. Is emerging as contaminant in water. In fact, it is highly soluble in water and adsorbs very weakly to soil particles. MIMs are advanced functional membranes with high specificity and selectivity toward a molecule of specific interest named template. This peculiarity is due to the presence of specific recognition sites in the membrane matrix, which are complementary to the template in chemical function, shape and size. These sites contains the molecular memory of the template. The molecular imprinting technique [2] to introduce them into a membrane is used.

The phase inversion technique for preparing MIMs from polymers *ad hoc* synthesized was used. Polyacrylonitrile and its co-polymers, with different functional co-monomers (acrylic acid, methacrylic acid, itaconic acid and acrylamide) were chosed as membrane forming material. Membranes were characterized by IR analysis, pure water water permeability and contact angle measurements. SEM analysis were also done. The membrane performance was evaluated by means of rebinding experiments aiming to determine the membranes affinity to the template molecules *versus* other structural analogues pesticides.

First, screening experiments were carried out in order to determine the best functional monomer able to interact with the template [3]. Subsequently, some advances of imprinting technique [4] for developing novel hybrid imprinted membranes with enhanced recognition properties towards dimethoate were employed. In this perspective, cross-linked imprinted polymer powders were hybridized with Poly(acrylonitrile-co-acrylic acid) co-polymer.

Results showed that the best functional monomer for interacting with the template was acrylic acid. Hybrid membranes exhibited high hydraulic permeability and selective recognition ability with respect to other kind of membranes.

Results of this wok suggest that dimethoate-imprinted membranes could be potentially employed for the detection and/or removal of this pesticide from polluted sites.

Key-Words Pesticides, molecularly imprinted membranes, selective recognition properties.

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O 14B – Optical detection of water pollutants/nanoparticles and their toxicity to living microorganisms

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Abstract

Purpose: The presence of pollutants in potable and river waters is monitored using either standard technologies which are time consuming, sophisticated and required costly instrumentation (e.g. chromatography) or by using advances (miniaturized) technologies like biosensor devices that are simple, rapid as response-time, less expensive, portable and highly sensitive and selective. Between different optical methods, chemiluminescent detection possesses several advantages including the lack of need of a light input, the relatively simple instrumentation required, a very low detection limit and a wide dynamic range. Herein, several protocols for improving the analytical performances of bioluminescence generated by genetically engineered *E. coli* in the detection of different toxicants (e.g. atrazine, carbofuran, nonylphenol and non-metallic nanomaterials) are discussed.

Experimental description: A first protocol using a two-stage bioluminescence reading approach (both were required): one for continuous monitoring of light evolution for 5 h (fresh stage investigation) and a second for another 5 h (after an overnight cold incubation at 4 °C) is proposed. A second protocol containing three major steps: incubation at 25°C, centrifugation and washing of aged bacterial cells with fresh LB medium is employed. A third protocol investigating the influence of different temperatures is used for the detection of nonylphenol. Interesting bioluminescent signal evolutions at 25°C and 30°C are recorded in the presence of carbonaceous nanomaterials (NPs) using two genetically engineered *E. coli* strains DPD2794 and TV1061.

Results: By using the above protocols, 0.01ng/mL atrazine, 0.5pg/mL carbofuran and 10fg/mL nonylphenol, respectively are detected. On another hand, three carbonaceous nanomaterials (MWCNT, graphene nanosheets and carbon black nanopowder) had similarly effect on *E. coli* TV1061 bacterial bioluminescence while *E. coli* DPD2794 can discriminate between different NPs concentrations.

Conclusions: Genetically engineered *E. coli* bacterial bioreporter strains are successfully used to evaluate the toxicity of atrazine, carbofuran, nonylphenol and three carbonaceous nanomaterials.

Key Words: water pollutants, nanoparticles, bioluminescent bacteria

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O 15B - An overview on the treatability of emerging micro pollutants by ferrate(VI) and resulting toxicity of the treated effluent

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Abstract

This speech will present an overview on the application of ferrate in the removal of emerging micro pollutants from water and wastewater with the scopes on the below issues:

1. Ferrate and its unique properties,
2. The feasibility of the use of ferrate to remove micro pollutants,
3. The formation of by products and the toxicity of the ferrate treated water and wastewater,
4. Potentiality of using ferrate for the treatment of micro pollutants.

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O 16B – Morphological engineering of thin film photocatalysts for air pollution abatement

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Abstract

Purpose: The goal of this research is the controlled fabrication of well immobilized, porous, highly performant TiO₂ films for use in photocatalytic degradation of gaseous organic contaminants.

Experimental description: Atomic Layer Deposition (ALD) was used for the controlled deposition of TiO₂ on carbon nanotubes and carbon nanosheet sacrificial substrates. The samples were annealed at 550°C in air in order to remove the carbonaceous substrates and to crystallize TiO₂ into the anatase phase. The performance of these samples was evaluated by the degradation of acetaldehyde in air at different flow rates and compared to a reference film of the commercially available PC500 photocatalyst. For this, a single-pass flow-through flat-bed photoreactor was used in connection with an automated gas setup.

Results: Carbon nanosheets and carbon nanotubes were used as templates for the engineering of photoactive TiO₂ films by means of atomic layer deposition. Calcination of the films at 550°C led to removal of the template (verified by EDAX) and transformation of the as-deposited continuous amorphous TiO₂ layers into a network of crystalline TiO₂ anatase nanoparticles (verified by XRD and TEM), commensurate to the original template morphology (observed by cross-section SEM). For both carbon nanotube and nanosheet substrates, an initial increase in photocatalytic activity was observed with increasing amounts of deposited TiO₂. An excess of TiO₂ led to dense films with lower performance. The optimum amount of TiO₂ deposited on carbon nanotubes was achieved after 100 deposition cycles, whereas the optimum for the carbon nanosheet templates was reached after 200 deposition cycles. All together, the former sample showed the highest activity. It was almost twice as efficient as a commercial TiO₂ reference film at a gas residence time as short as 0.15 s. Furthermore, its high photocatalytic activity was sustained even after ten test runs.

Conclusions: In conclusion, carbon nanotubes and nanosheets as sacrificial templates for atomic layer deposition can be used effectively for the controlled fabrication of well immobilized, thin, conformal, spacious and highly active TiO₂ films that perform very well in the gas phase photocatalytic degradation reaction of acetaldehyde.

Key Words: Photocatalysis, titanium dioxide, acetaldehyde, carbon nanotubes, carbon nanosheets, thin films

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O 17B - Levels of toxic arsenic species in native terrestrial plants from soils polluted by former mining activities

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Abstract

Arsenic is considered a toxic element for plants. However, the discovery of As resistant and hyperaccumulating plant species has increased the interest in understanding the distribution of As species in these environmental matrices. Although As can be present in plants under different chemical forms, such as phytochelatin, the As remained in plants as free inorganic (arsenate (As(V)) and arsenite (As(III)) or methylated ions has a greater interest due to its higher mobility and toxicity, and therefore, its ecological impact and risk to health.

The aim of this work consisted on the determination of the fraction of As present as toxic forms (inorganic and methylated species) present in native terrestrial plants from polluted soils by former mining activities (Mónica mine, NW Madrid, Spain), with high total As concentration levels (up to $3,500 \mu\text{g g}^{-1}$) [1], due to their higher mobility and the risk associated to their reintegration into other environmental compartments. Roots and aboveground parts were analyzed separately, to assess possible transformations from translocation processes. Extractions were carried out with deionized water by microwave-assisted extraction, at a temperature of 90°C and three extraction steps of 7.5 min each. Total extracted As concentrations were determined by ICP-AES, showing extraction percentages from 9 to 39%. Speciation studies were performed by HPLC-(UV)-HG-AFS [2], and they showed the main presence of As(V) (up to $350 \mu\text{g g}^{-1}$), followed by As(III), in both plant parts. Monomethylarsonic acid (MMA) and trimethylarsine oxide (TMAO) were also found only in some plants. On the other hand, the use of 0.5 mol L^{-1} acetic acid as extractant led to higher extraction percentages (33-87%), but lower column recoveries, probably due to the extraction of As compounds different to toxic free ions studied, which may come from biotransformation mechanisms carried out by plants to reduce As toxicity. However, As(V) concentrations increased up to $800 \mu\text{g g}^{-1}$ in acid medium, indicating the probable release of As(V) from organoarsenic compounds and therefore a higher potential risk for the environment [3]. From the easily soluble, water-extractable As species concentration levels, it can be drawn that between 70 and 89% of the total As in plants must have been biotransformed, so it is present under the form of different As compounds. Still, high As concentration levels remain as toxic forms, predominantly as As(V), reaching up to $190 \mu\text{g g}^{-1}$ considering roots and aboveground parts separately, and $350 \mu\text{g g}^{-1}$ considering the sum of both plant parts (more than double in acid medium), which may constitute an environmental risk due to its possible reintegration to the environment. Therefore, the study and control of native plants growing in As polluted soils is a relevant factor for environmental safe.

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Key Words: toxic arsenic species; microwave-assisted extraction; terrestrial plants; mining soils.

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O 18B – An eco-friendly approach for bioremediation of arsenics from contaminated water to protect human health and the environment

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Abstract

Purpose: The short-term goal of this work is to identify and study arsenic resistant bacterial strain(s) that can uptake and accumulate this toxic metal inside the cells thus reducing arsenic concentration in the contaminated source. However, the long-term goal of this work is to develop an eco-friendly and sustainable method for removal of arsenics from contaminated water to protect hundreds of millions of people worldwide from severe diseases caused by chronic water borne poisoning with arsenics.

Experimental description: The bacterial strain B1-CDA was isolated from an arsenic contaminated cultivated land in the south west region of Bangladesh. In this study we have used several modern techniques to qualitatively and quantitatively localize arsenics in the bacterial cells. Dynamic time of flight secondary ion mass spectrometry (TOF-SIMS) imaging and depth profiling have been employed to follow the distribution of arsenic ions within the cells. Inductively coupled plasma-mass spectrometry (ICP-MS) has been used to measure the amount of arsenic in the dry bacterial cells. The concentration of arsenics in the cell free broth has been measured by using the inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Results: To characterize this strain we have employed biochemical and scanning electron microscopy methods. The methods confirmed that the B1-CDA strain belongs to *Lysinibacillus sphaericus*. The minimum inhibitory concentration (MIC) value of this strain is 500 mM (As) as arsenate. TOF-SIMS and ICP-MS analyses confirmed intracellular accumulation of arsenics resulting reduction of this metal concentration in the growth medium. Arsenic accumulation in cells amounted to 5.0 mg/g of the cells dry biomass and thus reduced its concentration in the contaminated liquid medium by as much as 50%. We have also sequenced the whole genome of this strain and the genomic sequence has already been submitted in ENA database. Genomic analyses revealed that the genome of B1-CDA harbors several arsenic responsive genes. Three of the genes have been cloned and characterized. These results are in progress and will be discussed during the conference.

Conclusions: The results from these studies confirm that the bacterial strain B1-CDA has potential for reducing arsenics in the contaminated sources to safe levels. Therefore, the socio-economic impact of this research will

be highly significant for many countries worldwide especially in the developing world where impoverished families and villages are most impacted due to arsenic contamination. Besides human arsenic poisoning, this discovery will also benefit livestock and native animal species. Consequently, the outcome of this research will be vital not only for people in the affected area but also for human populations in other countries which have credible health concerns as a consequence of arsenic-contaminated water and foods.

Key Words: Pollution; Toxic metals; arsenics; bioremediation; bacteria; bioaccumulation.

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O 19B – Essential metal transporters expression and morphological appearance in cadmium-accumulated human placenta

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Abstract

A toxic heavy metal, cadmium (Cd) can cause various adverse effects on human organs, such as the placenta. Metallothionein (MT), a low-molecular-weight-cysteine rich protein, is a marker for Cd accumulated in tissues. Cd is able to be transported competitively by several essential metal transporters including calcium (Ca) channels.

Purpose: In this study, we aimed to investigate the Iron (Fe) transporters (TFR1, FPN1, DMT1), the Zinc (Zn) transporters (ZIP1, ZIP8, ZNT1), the Ca influx channels (CACNA1C) and the Ca efflux pump (PMCA1) expressions in human placentas with high MT expression and signs of morphological changes.

Experimental description: Fourteenth healthy pregnant women were included in the study after signing the informed consent forms. All placentas were immediately collected after normal labor. The Cd, Fe and Ca levels were measured by FT-AAS. The TFR1, FPN1, DMT1, ZIP1, ZIP8, ZNT1, CACNA1C, PMCA1, MT-1A and MT-2A mRNA expression levels were examined by RT-PCR. The protein expression and localization were studied by Western blotting and immunostaining, respectively. H&E staining was applied for examining histological changes.

Results: We found that placentas with high Cd levels expressed significantly higher levels of the MT isoforms MT-1A and MT-2A than placentas with low Cd levels (mRNA $p < 0.05$, protein $p < 0.05$). Also TFR1, DMT1, ZIP8, ZNT1 and CACNA1C mRNA were expressed at significantly higher levels. Only DMT1 and CACNA1C were significantly highly expressed at both, protein and mRNA levels ($p < 0.05$), whereas FPN1, ZIP1 and PMCA1 mRNA were not different. Moreover, syncytial knots and fibrinoid materials were highly aggregated in high-Cd level placentas.

Conclusions: We suggested that expression of MT-1A and MT-2A may be used as a Cd-marker in human placenta. It is possible that both Cd in maternal and fetal blood may be transported into the placenta via TFR1,

DMT1, ZIP8 transporters and CACNA1C, Ca influx channel resulting in high-Cd accumulation in the placenta and causing in cytotoxic effects and associated morphological changes.

Key Words: metallothionein, metal transporter, placenta, cadmium

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O 20B – Novel metabolic pathways of chlorinated cyclodiene pesticide dieldrin by *Mucor racemosus* strain DDF under aerobic conditions

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Abstract

Purpose: Dieldrin ($C_{12}H_8Cl_6O$; HEOD) is a chlorinated cyclodiene pesticide which has been used worldwide since 1940s. Although it is very efficient insecticides, its use has been prohibited in many countries since the 1970s because of its biological magnification, high toxicity and long persistence in the environment. Dieldrin was listed as one of the persistent organic pollutants (POPs) in the Stockholm Convention. *Mucor racemosus* DDF was isolated from upland soil annually applied with endosulfan and degraded approximately 90% of dieldrin (5 mg/L) during 10 days of incubation¹⁾. Although several dieldrin-degrading bacteria and fungi including strain DDF have been isolated to date, information on the metabolites and metabolic pathways is still limited. Therefore, the aim of this study is to identify the metabolites, and to propose novel metabolic pathways of dieldrin by fungus strain DDF

Experimental description: 1) Detection of initial metabolite. Strain DDF was grown in 500 mL of a modified Czapek-yeast liquid medium (MCD) containing 13.2 μ M dieldrin for 5 days. The whole culture was homogenized and separated into a mycelial fraction and a fluid fraction by centrifugation. The fluid fraction was acidified to pH 2.0 and extracted with ethyl acetate. The mycelial fraction was also extracted with ethyl acetate. The ethyl acetate extracts were mixed and evaporated to a state of dryness. The concentrate was resuspended into acetone/hexane (1:1) and was derivatized with BSTFA. Aldrin *trans*-diol in the BSTFA-derivatized concentrate was analyzed by GC/ECD. Aldrin *trans*-diol as a metabolite was confirmed by monitoring of the chlorination pattern using the selective ion monitoring (SIM) mode of HRGC-HRMS. 2) Detection of downstream metabolite. Pre-cultured fungal disks were inoculated into 10 mL of MCD at 25 °C under static culture. After 14 days, 50 μ L of aldrin *trans*-diol (1000 mg/L) in acetone was added to each culture. The cultures were homogenized with 10 mL of acetonitrile and were centrifuged. The supernatants were analyzed periodically by UPLC-ESI-MS system. The molecular ion peak at m/z 456.8 $[M+CH_3COO]^-$ indicated aldrin-*trans*-diol in negative ion mode, and other metabolites were detected in a range from m/z 300 to 500 in negative or positive ion mode.

Results: 1) In the ethyl acetate extracts of culture from strain DDF, a different peak with dieldrin was detected at the retention time of 7.39 min by GC/ECD. This peak was assigned as aldrin *trans*-diol on the basis of coelution with an authentic standard. The metabolite was detected at the retention time of 27.95 min, and its retention time and relative intensity of chlorination pattern matched those of the standard. 2) After 14 days, aldrin *trans*-diol was degraded by over 90% with strain DDF, while two metabolites were detected in negative ion mode. These metabolites showed the same isotopic pattern possessing six chlorine atoms. These were presumed to be sulfated or phosphorylated aldrin *trans*-diols because of their formula weight. Therefore, the candidate derivatives were synthesized and the retention times of the natural metabolite and the synthetic phosphate were compared. As a result of a co-injection experiment, the metabolites were determined to be aldrin *trans*-diol *exo*- and *endo*-phosphates. These results were also supported by HR-FAB-MS of the natural metabolite ($\Delta = 0.63$ ppm).

Conclusions: It is proposed that dieldrin was initially hydrolyzed to aldrin-*trans*-diol, and then aldrin-*trans*-diol was phosphorylated by strain DDF.

Key Words: dieldrin, POPs, fungus, metabolites, phosphorylation, UPLC-ESI-MS, HR-FAB-MS

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O 21B - The simultaneous biological removal of sulfur, nitrogen and carbon from industrial wastewaters: Performance and Modeling

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Abstract

Purpose: The simultaneous biological removal of sulfur, nitrogen and carbon process is a promising biological treatment for industrial wastewater due to its cost-effective, highly efficiency of contaminants conversion, and environmental friendly advantages.

Experimental description: The performance of simultaneous removal of sulfur (sulfate, 1000 mg/L), nitrogen (nitrate, 500 mg/L) and carbon (lactate, equal to 3000 COD mg/L) from synthetic industrial wastewater in continuous reactor and batch tests were investigated under anaerobic condition and micro-aerobic condition aiming to improve elemental sulfur recovery via sulfate reduction and sulfide oxidation. During continuous operation, the micro-aerobic condition was developed by the installation of a 5-L aeration tank on the internal circulation pipeline to provide trace oxygen at aeration rate of 0.5-6.25 mL O₂ min⁻¹ L_{reactor}⁻¹ and in batch tests limited oxygen addition was ranging from 20 to 100 mL to generate oxygen to sulfate-sulfur (SO₄²⁻-S) molar ratio (R_{OS}) of 0.39, 0.77, 1.16, 1.55, or 1.93.

Results: Under anaerobic condition, almost 100% of sulfate and nitrate, 30% of COD were removed and elemental sulfur recovery was only 11.1%; while under micro-aerobic condition, elemental sulfur recovery peaked at 69.2% with aeration rate of 1.0 mL O₂ min⁻¹ L_{reactor}⁻¹; 91.0% of sulfate, 100% of nitrate and 89.6% of COD in the influent were removed. Analysis of substrates conversion kinetics indicated that at limited-oxygen, the nitrate inhibition on sulfate reduction was relieved and sulfate reduction rate seemed relatively higher than that obtained without limited-oxygen fed, whereas kept almost constant cross the five R_{OS} states. In contrast, nitrate reduction rates decreased substantially with the increase in the initial limited-oxygen fed. Based on the kinetics analysis, a comprehensive mathematical model was developed to describe simultaneous biological removal of sulfur, nitrogen and carbon process from industrial wastewater by combination of ADM1 (organic carbon degradation coupled with sulfate reduction) and ASMs (heterotrophic denitrification and aerobic COD oxidation) accompanied with some extensions including oxygen/nitrate-driven sulfide oxidation processes, and oxygen was added into the model as a new component, well linking anaerobic and micro-aerobic biochemical reactions. The best estimated parameters were proven to be highly identifiable by analyzing the 95% confidence intervals of individual parameter estimates and the joint confidence regions for different

parameter combinations, which were calculated from the mean square fitting errors and the sensitivity of the model to parameters.

Conclusions: The simultaneous biological removal of sulfur, nitrogen and carbon successfully achieved highly efficient contaminants removal and elemental sulfur recovery which were significantly enhanced under micro-aerobic condition. The developed simultaneous desulfurization and denitrification model presented a practical tool for development, optimization and control of sulfur-nitrogen-carbon removal process.

Key Words: simultaneous biological removal of sulfur, nitrogen and carbon; sulfur recovery; industrial wastewaters; micro-aerobic condition; mathematical modeling

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O 22B - The potential ameliorative effect of Tiron and ascorbic acid against mercury chloride neurotoxicity in rabbit

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Abstract

Purpose: The current study was performed to assess the potential of 4-5 dihydroxy-1, 3 benzendisulfonic acid (Tiron) and L-ascorbic acid (vitamin C) against inorganic mercury (mercuric chloride-HgCl₂) induced oxidative stress and neurotoxicity in female New Zealand white rabbits.

Experimental description: Ten rabbits per group were assigned to one of four treated groups: 0 mg HgCl₂, 0 mg Ascorbic acid and 0 mg Tiron (control); 1mg Hg Cl₂/kg b.w orally; 1mg HgCl₂/kg b.w orally plus 1gm ascorbic acid /liter in drinking water ; HgCl₂/kg b.w orally plus 471mg Tiron/kg b.w I/P. Rabbits were administered HgCl₂ and ascorbic acid for three months while Tiron administered in 6 concessive doses for 15 days at the level of three doses per week. Biochemical analyses on oxidative stress-related parameters and acetylcholine esterase activity as neurotransmitter were carried out. Histopathological analyses for detecting the cellular damage in brain tissues of exposed rabbits were also performed.

Results: Results obtained showed that HgCl₂ significantly ($p < 0.05$) increased malondialdehyde and 4-hydroxyalkenals (MDA&4-HAE the marker of lipid oxidation) in brain tissues, while the activities of superoxide dismutase (SOD), glutathione peroxidase (GSHPx) and acetylcholine esterase (AChE) activities were significantly ($p < 0.05$) decreased. Histopathological analysis of brain revealed that neuronal degeneration with apoptotic features including cerebral cortex, hippocampus and the cerebellum. A significant ($p < 0.05$) decrease of purkinje cells number in cerebellum was detected. Also the purkinje cells lost the normal shape and became distorted. Most of the above parameters responded positively with either Tiron or vitamin C therapy, but more pronounced beneficial effects were observed in Tiron group than vitamin C group.

Conclusions: It is concluded that there is a protective effect of vitamin C as antioxidant and Tiron as a chelating agent against mercury chloride - induced neurotoxicity. Tiron was more effective than vitamin C in restoration of the most investigated parameters.

Keywords: Mercury; Oxidative stress; Neurotoxicity; Tiron; Vitamin C

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O 23B – Petrochemical companies cause bioaccumulation of heavy metals in aquatic organisms of contaminated regions: Threats and Solutions

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Abstract

Purpose: The effects of petrochemical company on the bioaccumulation heavy metals in Aquatic organism.

Experimental description: The concentrations of heavy metals in Persian Gulf are low, but petrochemical and refinery activities have caused an increase in heavy metal wastes, especially in coastal regions. The present study was done to determine the bioaccumulation of heavy metals in the muscle of white shrimp (*Litopenaeus vannamei*) using flame atomic absorption spectrophotometry. The experiment was conducted in four important coastal regions of the Persian Gulf: Bushehr (2 petrochemical sits), Deylam (without petrochemical site), Mahshahr (10 petrochemical sites), and Abadan (1 petrochemical site). Amounts of seven heavy metals such as Copper (Cu), Iron (Fe), Lead (Pb), Zinc (Zn), Nickel (Ni), Cadmium (Cd), and Cobalt (Co), were measured as lg/g heavy metal in dry weight in the muscle of white shrimp.

Results: The results of this study indicated that concentrations of Copper, Zinc and Lead in Mahshahr and Iron in Abadan and Nickel in Deylam had the highest concentrations in heavy metal. Cadmium and cobalt in all the locations had very negligible concentrations. Nickel in Mahshahr, lead in Deylam, and copper in Abadan and Bushehr had the lowest concentrations.

Conclusions: The shrimp market in Iran is dependent upon shrimp farming and harvesting from these regions. Therefore, it is strongly recommended that a monitoring system be deployed, especially in polluted areas. Stricter regulations for shrimp harvesting and farming could satisfy health and safety considerations in the shrimp market. This study revealed information that the primary risk for human health and the marine life chain was lead in the muscles of white shrimp in Mahshahr, where intense petrochemical and refinery activities are conducted. The high, hazardous levels of lead pollution in the shrimp of Mahshahr are alarming for authorities, since lead in the human body tend to cause deadly diseases.

Key Words: Bioaccumulation; Heavy metals; White shrimp; Spectrophotometry

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O 24B – Intelligent Systems for the Analysis of Environmental Pollutants

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Abstract

Key Words: Intelligent systems, fluorescence detection, artificial neural networks, pollutants, environmental control

There exist compounds daily used, like agriculture pesticides or organic substances and a large number of their adverse effects have been detected after decades of its application [1]. They are generally found in the environment as complex mixtures, having important environmental interest. Because of this, the resolution of difficult multi-pollutant mixtures is an interesting problem to be solved. The determination of these compounds is largely carried out using different analytical techniques [2]. These methodologies are relatively expensive, complex and time consuming. An important research area is the development of alternative and simple methods, with precise and sensitive detection. There are interesting endeavours using chemiometric and computational techniques as complementary approaches.

Our proposal is in the framework of computational approach. It consists in the use of intelligent systems for fluorescence detection of pollutants. This topic will allow introducing the intelligent environmental monitoring.

An intelligent system has characteristics and behaviour which can resemble to the human intelligence. Some of these characteristics are sensors, effectors, memory and its most appealing quality, the learning capacity. They learn from the experience, improving their performance and efficacy. This capacity gives the possibility to the intelligent system for planning the most appropriate actions for each situation to solve. They are flexible and adaptive. These characteristics allow adapting the intelligent system to different pollutant families, keeping a common structural base. This makes easier the development of general intelligent environmental control systems.

We focus our efforts developing intelligent systems based on artificial neural networks for the analysis of environmental pollutants. In these systems, the intelligence emerges from complex behaviour of the high interconnected process units, addressed by learning processes. We present in this paper several intelligent systems based on unsupervised neural networks and ensemble systems with data fusion schemes, for fluorescence detection of different pollutant families, Benzimidazole Fungicides and Polychlorinated

Dibenzofurans. The building block of these systems is the hierarchical unsupervised modular adaptive neural network HUMANN [3].

Figures of merit as precision, sensitivity and limit of detection, will be analysed in order to reach the optimal intelligent system configuration. A data set with synchronous and conventional fluorescence spectra and the clean sample have been used, from an experimental design with chemical and computational requirements [3]. Our proposal has allowed us to infer that the intelligent systems based on neural ensembles are the most efficient scheme for complex mixture resolution of up to 4 compounds. It also detects the absence of any pollutant. The synchronous fluorescence spectra provide the best information to face this problem. Finally we have shown the goodness of intelligent systems and fluorescence spectra as a smart and flexible alternative for environmental control.

Acknowledgements: We appreciate the support given and the data provided by Environmental Chemical Analysis Group at the Universidad de Las Palmas de Gran Canaria

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O 25B – Design of PVA-SA-*n*ZnO-*Jania rubens* (red algae), a hybrid nano bio-matrix for removal of lead: Characterization, kinetic and thermodynamic studies

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Abstract

Purpose: Amplification of biosorption capacity of *Jania rubens*, a red algae biomass by designing a bio-nano-matrix using polyvinyl alcohol (PVA) and Na-alginate (SA) blend for removal of Pb(II) and regenerated for several cycles. *n*ZnO, PVA and SA were used for metal oxide, thin film with physical strength respectively on the hybrid matrix.

Experimental description: 2% & 4% w/v of SA and PVA (SRL) blended and *n*ZnO 100 mg were added slowly to the solution and was sonicated for 30 min. *J. rubens* (pretreated with 1M HNO₃ at 60°C for 30 min) 4% w/v was added to the blend of polymer mixture and stirred for 30 min at 40°C. PVA-alginate-*n*ZnO-*J. rubens* uniform solution was added drop wise through peristaltic pump into 0.05M CaCl₂ 2H₂O & 10 w/v of Boric acid mixture present in beaker. The formed beads were cured with Boric acid mixture solution at 4°C for 24 h. The yield of 200 mL blended PVA-SA-*n*ZnO-*Jania rubens* uniform solution was determined as 200 mL of beads. Equilibrium studies carried out with matrix for removal of Pb(II) against parameters pH, biomass weight, temperature, initial Pb(II) concentration. Kinetic, thermodynamic and characterization studies were conducted on the biomatrix. Adsorption-desorption studies were performed with 2N HCl for 4 cycles.

Results: FTIR results shown -OH, -C-N, -C-O, -C-N-C, -CO-NH, and -C-OH were intensely involved in the biosorption process. SEM results reveals that the film like entrapment of biomass and plenty of pores can enhance the Pb(II) ions adsorption on the matrix. The metal uptake was rapidly increased within the 1 h and slowing down as the equilibrium is attained at 2 h. pH increase from 3 to 5 increases metal uptake from 23.21 to 39.09 mg g⁻¹ and a fall in uptake at pH 6. PVA-SA-*n*ZnO-*J. rubens* matrix q_e increased from 10.10 to 39.09 mg g⁻¹ with increasing metal concentration from 24.86 to 98.75 mg L⁻¹ at sorbent dose of 2 g L⁻¹ with pH 5 at 30°C. The up taking capacity of Pb (II) was declined from 39.09 to 11.31 mg g⁻¹ at a pH of 5 and the % removal of Pb(II) increased from 75.17 to 90.68 when increasing the biomass dosage from 2 to 8 g L⁻¹. The data is fitted well with Langmuir model isotherm, q_{max} is 111 mg/g and R_L values are in the range of 0-0.3. The sorption kinetics following pseudo-second-order kinetics and the process is endothermic, spontaneous in nature.

Desorption study reveals that the % removal of Pb(II) is decreased from 91.3 to 78.3 at 3rd Cycle and at 4th it was 61.63%.

Conclusions: The equilibrium was achieved in 2 h for PVA-SA-*n*ZnO-*Jania rubens* with Pb(II). The q_{\max} is 111 mg/g, the process is endothermic in nature. The matrix efficiently entrapped the biomass and shown more pores for adsorption of Pb(II) ions. -OH, -C-N, -C-O, -C-N-C, -CO-NH, -NH₂, -SH, and -C-OH were intensely involved in the biosorption process. The optimum pH is 5, biomass weight is 2g/L. The data is well described by pseudo-second-order kinetics and fitted well to Langmuir isotherm model. The regeneration studies revealed that PVA-SA-*n*ZnO-*Jania rubens* matrix can be efficiently used for 3 cycles without significant loss of biosorption capacity.

Key Words: bio-matrix, metal oxides, *J. rubens*, FTIR, SEM.

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O 26B – Source identification and potential ecological risks of organic (hydrocarbons) and inorganic (metals) contaminants in sediments of aquatic ecosystems: Case studies of Southeastern Brazil

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Abstract

Purpose: The main purpose of the present work is to review the major findings on source identification, biogeochemical processes and potential risks of organic (hydrocarbons) and inorganic (metal) contaminants in sediments of aquatic ecosystems from Southeast region of Brazil. These results were surveyed extensively by our research group over the past decade or so, in several case studies such as the cascade of hydroelectric reservoirs (QualiSed Project) and the Monjolinho River in São Paulo State and at the Ibitité reservoir and the São Francisco river in the State of Minas Gerais.

Experimental description : Surface sediment samples were collected from various sites in these ecosystems using a Birge-Ekman dredge. Samples were maintained refrigerated until sieved (2 mm) for chemical procedures. Polycyclic aromatic hydrocarbon (16 priority PAHs) and n-alkanes (C10 to C40 including isoprenoids pristane and phytane) were extracted according to USEPA method 3550B with a mixture of hexane/acetone in an ultrasonic bath (Ultra Cleaner 4800, 40 kHz and 220W—Unique, Brazil). Extracts were purified based on the USEPA method 3630C using a glass column packed with activated silica gel. PAHs were determined according to the USEPA method 8270D using gas chromatography coupled to a quadrupole mass spectrometer (GC-MS) and the aliphatic hydrocarbons in the GC-MS operating in SCAN mode. Total bioavailable metal fractions were extracted from sediment samples using the USEPA method 3050B and concentrations were determined using an atomic absorption spectrophotometer and a plasma emission spectrometry (ICPOES). AVS (acid volatile sulfide) analyses were performed by using wet samples and its contents were determined by methylene blue method in a closed line with gaseous nitrogen as carrier gas. SEM (sequential extracted metals) were analyzed by the various atomic absorption spectrophotometric techniques.

Results : Our results obtained from different sites dominantly showed hydrocarbon concentration values below TEL (threshold effects level) (with a few exceptions to this level and even less to the PEL, probable effects level). Therefore, toxicity to the benthic community may not be expected. Several distribution indexes calculated with the PAHs and n-alkane data pointed towards the classical main sources of these compounds, that is, biogenic, petrogenic and pyrogenic sources. With respect to metal concentrations, measured results

were compared to various classical sediment quality guidelines (SQG) (empirical SQG's: TEL, PEL and SEL and partition equilibrium SQG's: AVS-SEM and pore water toxic units). In some cases potential toxicity to benthos may be assigned to metals.

Conclusions : Main sources of hydrocarbons in studied ecosystems are biogenic, petrogenic and pyrogenic while of metals are industrial activities and urban surface runoff. Ecological risks in these sites are restricted to a very few potential cases in which SQG's have been violated. In a significant number of study sites, toxicity to the benthic community is due to the extremely high concentration of ammonium ions rather than the contaminants dealt in these works. Watershed, aquatic ecosystems and water quality managements are highly dependent to an integrated sediment quality scheme which in a holistic manner associate and interpret biogeochemical, biological in situ and ecotoxicological data sets.

Keywords: Organic and inorganic contaminants; Sediments; Ecological risk; Sources.

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O 27B - Molecular characterization at the gas/particle interface of soot generated from a diesel engine fueled with conventional and alternative fuels using a titration method

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Abstract

Purpose: Surface functional groups of two different types of combustion aerosol samples, a conventional diesel (EN 590) and a Hydrotreated Vegetable Oil (HVO) soot, have been identified and quantified using heterogeneous chemistry (i.e. gas-particle surface reactions). A commercial sample of amorphous carbon (PRINTEX XE2-B) was analyzed as a reference substrate.

Experimental description: Diesel and HVO soot samples have been recovered from a four cylinder, four stroke, turbo-charged, intercooled, common rail, 2.0 L Nissan diesel engine (model M1D), fulfilling Euro 5 emission regulations. Experiments on heterogeneous chemical reactions between a gas-phase probe molecule and a specific functional group on the surface of a soot sample, have been carried out in a Knudsen flow reactor.

Results: In comparison to the reactivity of amorphous carbon PRINTEX XE2-B the investigated HVO and diesel soot samples had a significantly higher surface density of reducing functional groups reacting with the O₃ probe gas by a factor of 10 to 30. Noteworthy is the fact that these reducing groups were practically all strongly-reducing because the O₃ and NO₂, figure 1, probe gases resulted in identical surface densities which may elicit distinct catalytic redox reactions in biological systems and may lead to unexpected health effects.

Conclusions: We state that NO₂ as an oxidizer readily reacts with strongly reducing surface functional groups of diesel and HVO soot. Based on the abundance and high fraction of strongly reducing surface functionalities in diesel and HVO soot we expect high antioxidant consumption in biological systems accompanied by a rapid onset of oxidative stress owing to a strongly reducing surface composition of the corresponding nanoparticle surfaced.

Key Words: Diesel, Hydrotreated Vegetable Oil, soot, Knudsen cell

Acknowledgements: This work was supported by project COST CM0901 “Detailed Chemical Kinetic Models for Cleaner Combustion”. Neste Oil and Repsol are acknowledged for the supply of HVO and diesel fuels, respectively.

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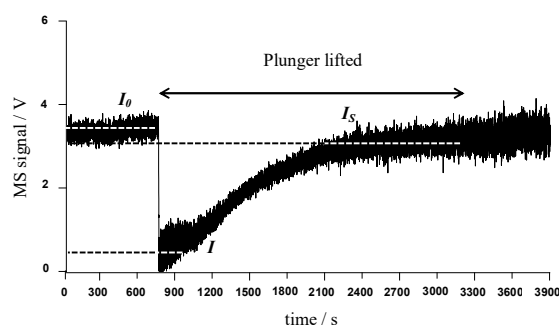


Figure 1. Raw data of NO₂ uptake on 16.4 mg Diesel soot at a flow rate of 1.13×10^{16} molecules s⁻¹ monitored at m/z 46 in the 1 mm diameter aperture.

O 28B - Discharges, emissions and losses of dangerous and hazardous substances: Risk assessment for water resources

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Abstract

The handling of chemicals, from industrial processing to daily home activities, can involve abnormal situations that can lead to releases following the contamination of surface water and groundwater. When persistent, bioaccumulative and toxic (PBT) substances are present the risk posed by this accidents can be

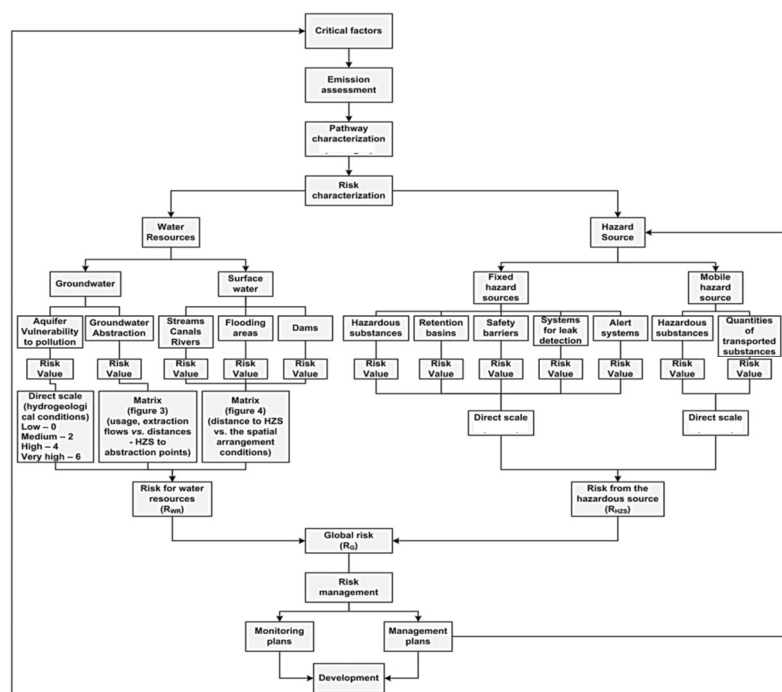


Fig. 1 - RAMWR (in Rebelo et al., 2014)

significant. To deal with the discharges, emissions and losses of dangerous and hazardous substances to water resources was developed a simple conceptual model based on a multi-criteria approach to provide rapid responses to support competent authorities on decision making. This model (fig. 1) was named Risk Assessment Model for Water Resources (RAMWR) and is based on the general methodologies on Environmental Risk Assessment (ERA) supported on strategic assessment procedures and uses of geographic information systems (GIS) for the spatial appraisal of the hazards and to identify risk receptors

(water resources). The model was applied to a real accident scenario in a facility for fuel oil storage and pre-heating located in Algarve which allowed well supported technical decisions in response to the situation. The RAMWR strength is its simplicity which allows to follow real situations ensuring that several options are appraised to achieve risk minimisation. The use of GIS helps to provide rapid information with accessible outputs.

Key Words: Risk assessment. Water resources, Hazards, PBT

Acknowledgements: The authors gratefully acknowledge the Portuguese Environment Agency and the European Regional Development Fund (FEDER), Programa Operacional Factores de Competitividade-

COMPETE, and the project PEst-OE/CTM/UI0195/2011 e Fundação para a Ciência e Tecnologia (FCT), for their financial support.

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O 29B – Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater

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Abstract

Contamination of water with toxic metal ions is becoming a severe environmental and public health problem. Thus, rising demands for clean and safe water in extremely low levels of heavy metal ions make it greatly important to develop improved technologies for heavy metal ions removal. Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology. Advantageously, the manipulability of magnetic nanoparticles by an external magnetic field gradient opens up many applications involving the environmental area. In this way, we propose maghemite nanoparticles (MNPs) functionalized with glycine, by a cost-effective and environmentally friendly procedure, as an alternative route to typical amine-functionalized polymeric coatings, for highly efficient removal of copper ions from water. In the present work, a series of experiments of glycine adsorption on MNPs from aqueous solutions at different initial concentrations and pHs were performed. To elucidate the interaction between glycine and maghemite during adsorption, several techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), magnetization measurements, dynamic light scattering (DLS), Fourier transform infrared (FTIR), and thermogravimetric analysis (TGA) were employed. Thus, the applicability of amine-functionalized MNPs in the removal of Cu^{2+} was evaluated in the view of pH, time and adsorbate/adsorbent concentrations. The adsorption kinetics and adsorption isotherms were investigated by using the conventional models of adsorption. Using an aqueous method of co-precipitation 12 nm sized maghemite nanoparticles were synthesized. Besides, it was observed that glycine is best adsorbed at pH ~ 6 and that saturation of oxide surface occurs with at least one monolayer of ligand, when glycine concentration reaches about 10 % (w/w) on functionalized nanoparticles. Specifically, the carboxylate groups of glycine strongly coordinate to iron cations on the maghemite surface to form a robust coating, while the functionalized exteriors (amino groups) remained in the water medium. It has been observed that these glycine-modified MNPs have strong affinity for the Cu^{2+} , probably due to electrostatic attraction and complexation of copper with NPs surface. The adsorption kinetics, highly dependent on the pH of the medium, followed a pseudo second-order mechanism. The adsorption equilibrium followed a Langmuir isotherm, giving a very high maximum capacity of copper adsorption. More specifically, our results suggest that these surface engineered magnetic nanoparticles are highly effective, efficient and economically viable magnetic nanoadsorbents for the removal of copper – and can be extended to other metals since amine groups present high binding affinity for metal complexation – from water in comparison to the existing industrial purification processes. Furthermore, these magnetic nanoadsorbents may be separated easily from the solution with the help of an external magnetic force and are reusable after removing the adsorbed toxic contaminants.

Key Words: magnetic nanoparticles; glycine-functionalized; wastewater; copper adsorption

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O 30B – Occurrence of PCBs and PBDEs in two dolphin species (*T. truncatus* and *S. frontalis*) from the Brazilian coast

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Abstract

Purpose: The monitoring of POPs in cetaceans has been mainly conducted in the Northern Hemisphere. However, little is known about the sources and fate of these pollutants in developing countries, where these compounds could still be in use. In this context, the aim of this study was to determine PCBs and PBDEs levels in liver samples of Bottlenose dolphins (*T. truncatus*) (n = 4) and Atlantic spotted dolphin (*S. frontalis*) (n = 6) from the Southeastern Coast of Brazil (Rio de Janeiro State) in order to increase data regarding these compounds in the Southern Hemisphere.

Experimental description: Approximately 1.0 g of homogenized and freeze-dried sample was used in this study. The analytical procedure was performed based on an Ultra Turrax Extraction, described previously by De Boer et al. (2001) with minor changes proposed by Quinete et al. (2011), consisting in three basic steps: Extraction, Clean-up and Chromatographic analysis. PCB 103 and 198 were used as standard surrogates and TCMX was used as internal standard for chromatographic analysis.

Results: PCBs ranged from 3.08 µg g⁻¹ to 15.31 µg g⁻¹ (lipid wt) in *T. truncatus* and from 2.51 µg g⁻¹ to 23.75 µg g⁻¹ (lipid wt) in *S. frontalis*. PBDEs varied from 71.34 ng g⁻¹ (lipid wt) to 132.96 ng g⁻¹ (lipid wt) in *T. truncatus* and from 84.55 ng g⁻¹ (lipid wt) to 165.09 ng g⁻¹ (lipid wt) in *S. frontalis*. PCB 153, 138 and 180 were the major PCB congeners detected in both species. Furthermore, BDE 47 was the major PBDE congener found in both species. The contamination patterns suggest the previous use of Aroclor 1254, 1260 and Penta-BDE mixtures in Brazil.

Conclusions: PCBs and PBDEs were never produced in Brazil. However, the concentrations found in the present study are of great concern, suggesting the presence of a source contamination in the Coast of Rio de Janeiro and representing a risk to these cetacean species.

Key Words: *Tursiops truncatus*; *Stenella frontalis*; PCBs; PBDEs; upwelling system; Brazil.

Acknowledgements: This study was financially supported by CNPq, CAPES and FAPERJ and conducted in collaboration with the Institute of Oceanography of the São Paulo University.

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O 31B – Nitrogen converters in wastewater treatment plants

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Abstract

Nitrogen removal is usually performed using the biological processes of nitrification and denitrification. In large wastewater treatment plants, this process is realized using biological nutrient removal (BNR) processes. All biological nitrogen removal in the activated sludge process takes place in two sequential reactions an aerobic stage (for nitrification) and an anoxic stage (for denitrification). Nitrification is a two-step process, consisting of the conversion of ammonia to nitrite, which is in turn converted to nitrate. In recent years, a multi-disciplinary team of scientists and engineers has been working to improve the performance of biological nutrient removal systems with the aim of optimizing the operations of existing plants, and has been investigating the implementation of new methods or technologies to achieve better treatment performance. The team is also focused on the diversity and activity of microorganisms involved in biological nutrient removal systems. Until recently, nitrification/denitrification was considered the only way of removing nitrogen from wastewaters. However, recent developments related to the microbial ecology have identified new players in the nitrogen cycle.

Anaerobic ammonia oxidation, a microbial process that was recently discovered in a denitrifying pilot plant reactor in Delft, involves the oxidation of ammonia to dinitrogen gas with nitrite as the electron acceptor under anoxic conditions. Since this discovery, Anammox bacteria have been detected in a variety of natural environments, such as marine sediments, an anoxic basin in the Black Sea, Arctic sea ice, subtropical mangrove sediments, tropical freshwater systems and wastewater treatment plants. The recent discovery of a new player, ammonia-oxidizing archaea (AOA), has upended the century-old dogma that nitrification can be achieved only by the domain of bacteria. Moreover, some scientists have indicated that the abundance of AOA can be significantly greater than their well-known bacterial counterparts in soil. It has also been suggested that most mesophilic Crenarchaeota are AOA and that these organisms are the numerically dominant ammonia oxidizers in the ocean. AOA have been identified in different natural environments, such as suboxic water columns, estuarine sediments, hot springs, ocean, soil ecosystems, and wastewater treatment bioreactors.

Nitrogen removal mechanisms in wastewater treatment plants (WWTPs) and the microbial communities involved in these processes can be better understood through the use of molecular tools. Molecular studies on nitrogen-converting microorganisms have improved the understanding of the diversity and evolutionary

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history of microbes involved in nitrogen removal. However, quantitative data on the abundance of specific microbial groups in WWTPs are still lacking. This study monitored and quantified nitrogen-converting microorganisms (AOB, NOB, AOA, and Anammox) simultaneously in different full-scale WWTPs.

Key Words: Nitrogen converters, molecular techniques, wastewater treatment plant

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O 32B – Harnessing mixed species microbial communities for use in ex situ naphthenic acid and PAH bioremediation

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Abstract

Purpose: Through a process known as bioremediation, tolerant microbes with specialized abilities to degrade pollutants may be utilized to mitigate pollutant exacerbations in the environment. How one harnesses and manipulates the available microbial communities to achieve bioremediation of target pollutants has important implications on the success of the bioremediation strategy. Biofilms are well known for their multifaceted tolerance to various pollutants. We hypothesized therefore that biofilms, cultivated directly from a contaminated environmental source, might be a choice strategy to harness microbes for use specifically in ex situ biodegradation of naphthenic acids (NAs) and polycyclic aromatic hydrocarbons (PAHs).

Experimental description: This study examined the cultivation (and NA and PAH degradative capacity) of both mixed and single species biofilm and planktonic cultures from contaminated environments. Scalability of the proposed mechanism to harness targeted microbial communities was also evaluated through application to existing moving bed biofilm reactor (MBBR) technology.

Results: Mixed and single species cultures derived from contaminated water and soil samples were capable of growing in the presence of synthetic mixtures of their respective contaminants, (NAs or PAHs) as determined by confocal microscopy and 16S rDNA qPCR. Single species cultures degraded markedly fewer NAs than mixed species communities. While contrary to the hypothesis, biofilm and planktonic mixed communities exhibited comparable NA degradation. The initial microtiter device used to grow biofilms was successfully up scaled, and applied to existing MBBR, wastewater treatment technology. Overall, microbial communities were better able to degrade PAHs, although this varied for each soil inoculum source.

Conclusions: The results of this study suggest that the ability to harness a diverse community of microbes from the environment as opposed to individual organisms is key for obtaining a population effective for ex situ biodegradation of NA and PAH hydrocarbons. Additionally, growth as a biofilm affords practical and logistical advantages making it more feasible to apply these communities in current ex situ (MBBR) bioremediation technologies.

Key Words: biofilms, bioremediation, naphthenic acids, PAHs, biodegradation, bioreactor, MBBR

Acknowledgements: This work was generously supported through grants from the National Science and Engineering Research Council of Canada, and Imperial. Imperial is also thanked for providing PAH contaminated soil samples, while an undisclosed oil sands operator is thanked for their in-kind contribution of oil sands process water.

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O 33B – A larger positive $\delta^{53}\text{Cr}$ shift from pollution source to groundwater at Czech industrial sites, compared to the northeastern U.S.

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Abstract

In polluted aquifers, spontaneous reduction of toxic, soluble Cr(VI) to largely insoluble, non-toxic Cr(III) may occur, depending on the availability of reductive agents. The reduction of Cr(VI) is associated with an isotope fractionation, with the product, Cr(III), becoming isotopically lighter. Seven industrial sites in the Czech Republic (Central Europe) and one in the northeastern U.S. were selected to study possible self-attenuation of Cr-polluted groundwaters. Cr-rich groundwaters at five Czech sites originated from electroplating (Loučna nad Desnou, Zlaté Hory, Letňany, Site B, and Bruntal). Chromium pollution at site Trutnov was caused by leather processing, at site Hradek nad Nisou resulted from production of Cr(III) salts. At the eighth study site (confidential upon request by owner; Connecticut, U.S.A.), Cr from electroplating was released to the environment in a dissolved form, but also by washdown of deposited aerosols. Direct sampling of the Cr in the industrial operations showed that $\delta^{53}\text{Cr(VI)}$ of the pollution source was low, $< 1\text{‰}$ [1]. $\delta^{53}\text{Cr(VI)}$ of the groundwaters was nearly always higher than the pollution source. At the Czech sites, $\delta^{53}\text{Cr(VI)}$ of the groundwaters ranged between 0.5 and 6.0 ‰, peaking at about 3 ‰. In contrast, at the U.S. site, $\delta^{53}\text{Cr(VI)}$ of the groundwaters was lower, ranging between 0.5 and 2.5 ‰. It appears that spontaneous removal of the toxic form of Cr from the groundwaters was under way in both countries. Higher $\delta^{53}\text{Cr}$ values of the residual Cr(VI) in Czech groundwaters may indicate a greater degree of Cr(VI) reduction, compared to the U.S. site.

[1] Novak M. et al. (2014) Environ Sci Technol. 48, 11, 6089-6096.

Key Words: chromium, isotopes, groundwaters, Cr pollution, fractionation

Acknowledgements: This work was supported by Czech Science Foundation (Grant no. P503/15-21373S to M.N.)

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O 34B – The fate of radiocesium deposited on trees by the Fukushima accident: Uptake and accumulation of radiocesium by trees

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Abstract

A huge earthquake hit the north-eastern area of Japan on March 2011, following which the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) was involved in the most serious nuclear accident since Chernobyl in 1984. As a consequence, a broad area of around 8900 km² was contaminated with more than a restrictive level (37 kBq m⁻²) of radioactive cesium. At the present time, 4.5 years since the accident, a part of the contamination has disappeared due to natural decay, but the remainder still presents a danger of increased radiation exposure. Forests cover most of the contaminated areas, and no decontamination plan has been undertaken yet. Therefore, there is a need to monitor the movements of the contaminants and determine whether they should be expected to flow to residential and agricultural areas, and if so, what effect they might have there.

We are one of the most active groups monitoring the radiocesium fate in the environment after the FDNPP accident. For example, yearly reviews of radiocesium contamination have been observed for more than 10 popular practical/ornamental woody species in Japan (e.g., *Pinus densiflora*, *Cryptomeria japonica*, and *Prunus x yedoensis*). Specific sampling of tree parts (leaves, twigs, and boughs), development years, and heights (bottom to top of each crown) has continued in Abiko (approximately 200 km SSW from the FDNPP) during periods of vigorous growth in each year after 2011. The changes in radioactive cesium concentration are always observed with that of the potassium concentration. In addition, litterfalls of the monitored species are also collected before they touch the ground. The flow of radiocesium via litterfall is being analyzed with particular attention to a natural arboraceous activity: autumnal nutrient resorption. On the other hand, the effect of the degradation of litterfall by microorganisms on radiocesium fluidization is also a target of our investigation. Two types of degradation experiments of litterfalls, natural and accelerated ones, are adopted to see the fluidization effect. This will be determined by chemical analysis of high molecular weight organic substances, such as fulvic and humic acids. In this presentation, some keys to understanding the fate of the radiocesium deposited on trees by the Fukushima accident will be discussed using the latest data.

O 35B – *In vivo vitellogenin* expression in male medaka induced by wastewater is determined by the balance between estrogenic and antiestrogenic activities

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Abstract

Purpose: Recently, growing number of studies using *in vitro* estrogen receptor (ER) reporter gene assay have reported that estrogenic and antiestrogenic activities coexist in wastewater. In a previous study, we demonstrated that the assay represents net estrogenic activity in the balance between estrogenic and antiestrogenic activities in wastewater. However, the *in vivo* effect of antiestrogenic activity in wastewater remained unclear. In this study, we investigated whether *in vivo* estrogenic effect of wastewater is affected by antiestrogenic activity. We also investigated whether the medaka (*Oryzias latipes*) ER α assay can predict the *in vivo* estrogenic effect in male medaka better than the human (*Homo sapiens*) ER α assay.

Experimental description: We measured the estrogenic and antiestrogenic activities of wastewater and reclaimed water by the *in vitro* ER α reporter gene assay (medaka ER α and human ER α); the expression of *vitellogenin-1* (*vtg1*) and *choriogenin-H* (*chgH*) in male medaka by quantitative real-time PCR; and estrone, 17 β -estradiol, estriol, and 17 α -ethynylestradiol concentrations chemically to predict estrogenic activity. By comparing these indicators, we investigated whether *in vivo* estrogenic effect of wastewater is affected by antiestrogenic activity.

Results: The net estrogenic activity measured by the *in vitro* medaka ER α reporter gene assay showed stronger correlation with the *in vivo vtg1/chgH* expression in male medaka than the concentrations of estrogens. The *in vitro* medaka ER α reporter gene assay also showed stronger correlation with *in vivo vtg1/chgH* expression in male medaka than the human ER α reporter gene assay.

Conclusions: *In vivo vtg1/chgH* expression in male medaka is determined by the balance between estrogenic and antiestrogenic activities. The *in vitro* medaka ER α reporter gene assay also predicted *in vivo vtg1/chgH* expression on male medaka better than the human ER α reporter gene assay.

Key Words: Mixture effect, estrogenic activity, antiestrogenic activity, wastewater, reporter gene assay, *vitellogenin* expression

Acknowledgements: This work was supported by a UK-Japan cooperative project of the Ministry of the Environment, Japan; the Japan Science and Technology Agency's Core Research for Evolutional Science and Technology (CREST) research promotion program; and grants from the Ministry of Education, Culture, Sport, Science and Technology.

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O 36B – Growth of streptomycetes in soil and impact on bioremediation

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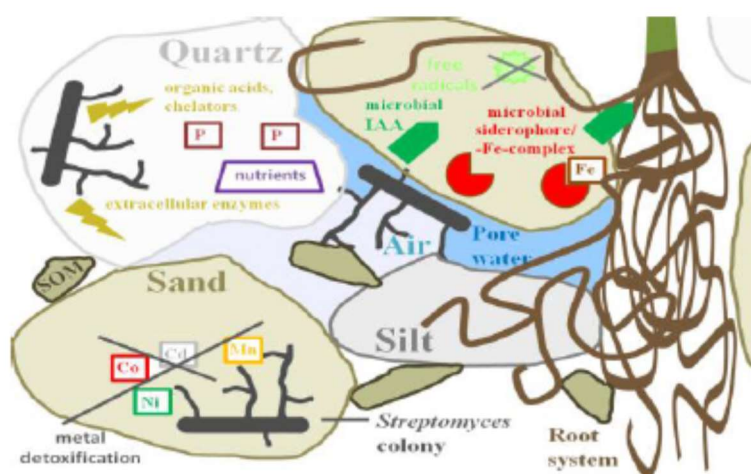
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Abstract

Purpose: Streptomycetes are Gram-positive bacteria that feature a filamentous growth, with aerial mycelium for exospore formation and distribution through the air. The filamentous growth is an adaptation to grow in soil shared with fungi. These bacteria are well known for their versatile metabolism, e.g. they produce 80 % of the antibiotics used in pharmacy. Their high adaptability to varying soil conditions allows them to dominate microbial communities under stress conditions like heavy metal contamination. We wanted to investigate mechanisms of heavy metal resistance to gain better understanding of the dominance in acid mine drainage influenced, poor soils. Adding plant growth promoting features investigation, we used strains to improve plant growth for bioremediation purposes in our test field site in the former uranium mining are 'Wismut' in Germany.

Experimental description: Investigation of growth with metals, biomineralization capacity, production of siderophores, survival in soil and production of phytohormones, phosphate mobilization and nitrogen fixation allowed to identify strains for microbially aided phytoremediation in heavy metal contaminated soils.



Results: Mechanisms for metal resistance included extracellular and intracellular defense strategies. Sequestration to the cell surface and chelation by siderophores able to bind metal ions, as well as production of melanin-like pigments and catalysis of biomineral formation were the main extracellular mechanisms involved in both, streptomycete metal resistance and altering plant metal uptake. Intracellularly, production of metallothioneins, reactive oxygen defense molecules like superoxide dismutase, and changed transcriptome and proteome profiles were observed. Additional features that promote plant growth allowed for application with a phytostabilization regime.

Conclusions: Our approach allowed for the production of biomass on heavy metal polluted soils, otherwise not useful for farming. At the same time, the plant cover will minimize metal input into groundwater, further protecting the area from ecotoxicological risks.

Key Words: bioremediation, metal resistance, siderophores, plant growth promotion, soil

Acknowledgements: We thank Prof. Dr. Georg Büchel and Dr. Dirk Merten, Friedrich Schiller University, Institute of Geosciences, for analysis of metals and Dr. Ales Svatos, Max Planck Institute for Chemical Ecology, for analysis of siderophores.

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Schütze et al., 2013. *Biogeosciences* 10, e3605-3614

O 37B – Emerging organic contaminants in groundwater in urban areas

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Abstract

Purpose: As techniques improve more microorganic compounds are emerging into the groundwater environment. These include pharmaceuticals and personal care products (PCPs), lifestyle compounds, such as caffeine, food additives and a range of metabolites. Environment Agency data shows that some emerging contaminants (ECs) are being frequently detected in groundwater, although few are at present considered under the WFD. The aim of this work was to evaluate the types and concentrations of ECs in groundwater beneath contrasting urban areas.

Experimental description: Samples were collected from boreholes and multi-level piezometers using a pump or depth sampler made from inorganic materials and analysed by the Environment Agency National Laboratory Service using a targeted GCMS screening method.

Results: Sources in the urban environment include wastewater and industrial effluent leakage and landfills (Figure 1). Groundwater from cities on the UK Sherwood Sandstone aquifer indicate that microorganics, including ECs, are present at depth in the aquifer (>50 m). The number of compounds detected down the depth profile appears to be a useful tool for assessing contamination and is consistent with chloride concentrations and earlier work on pathogens, suggesting a sewage source. For the Thames floodplain at Oxford the urban impact can be distinguished from a landfill plume using emerging contaminants. For the developing town of Kabwe in Zambia the pressures on the shallow groundwater system are from unsewered sanitation.

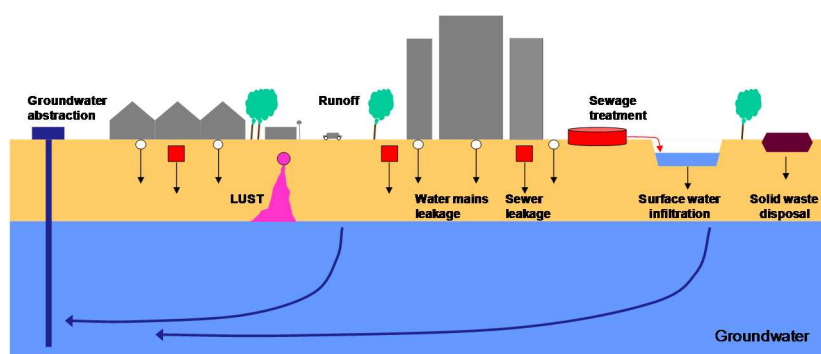


Figure 1. Sources of microorganisms in the urban environment and pathways to

Conclusions: Collecting good samples for these compounds is testing due to the wide range of potential sources, including sampling equipment and borehole casing. In long-established cities of the UK, ECs can be detected at depth in groundwater. We may see increasing PCPs and industrial chemicals as low income counties develop. Whilst some ECs are probably no threat to drinking water at such $\mu\text{g/L}$ concentrations, there is little information on their impact on other groundwater receptors in the environment.

Key Words: Groundwater; urban;

Acknowledgements: Environment Agency National Laboratory Service, Peter Williams and Birmingham University MSc students Stephanie Allcock and Nicola Moorhead for sample collection

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O 38B – Synergistic design of photocatalytic materials and processes

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Abstract

Purpose: Heterogeneous photocatalysis represents an efficient path for removing traces of toxic and recalcitrant pollutants from wastewaters, eventually getting the treated water ready for re-use. Thousands of materials are reported as being performant in heterogeneous photocatalysis, yet there are no industrial processes based on this process and the reports on pilot installations are scarce. The main reasons are related to costs (the UV-activation of most of the catalysts and their costs) and to durability in the working conditions. Based on these assumptions, the paper proposes a novel tandem thin film (SnO₂/Cu_xS-Cu_xO/TiO₂) that allows Vis activation; the main process parameters with influence on the durability are further investigated: pollutant concentration, pH, process duration, interim steps for catalyst recovery.

Experimental description: the oxides in the thin film were obtained from inorganic precursors (chlorides) while the sulfide was obtained also using thiourea. Spray pyrolysis was used for the sequential deposition of the three layered films. XRD, SEM and EDX, AFM and contact angle measurements were used to observe the composition, crystallinity and surface morphology/energy of the thin films. Photocatalytic experiments used methylene blue (MB) as reference pollutant. Experiments aimed at optimizing the pollutant concentration, the process pH (in the range: 3...12), the process duration (up to 72 hours) and were performed in static regime, under simulated solar radiation (85% Vis and 15% UV in the power of the irradiation source).

Results: the results outline that Cu_xS undergoes partial oxidation and supports obtaining a thin film that allows extended charge carriers flow, thus reducing recombination. Surface charge control by optimizing the pH might support the pollutant adsorption, as a beneficial first step in photocatalysis; however, photo-corrosion limits this control tool. Transmittance measurements before and after photocatalysis gave evidence on films (lack of) stability and allow optimizing the working pH. Long duration photocatalytic experiments gave evidence on surface clogging (with MB but also with the end-products, including the gaseous ones). An interim washing step was able to almost fully recover the photocatalytic activity, measured as variation in the total organic carbon and total nitrogen removal.

Conclusions: The results show that the SnO₂/Cu_xS-Cu_xO/TiO₂ thin films have the best efficiency and photo-corrosion resistance at neutral pH (TOC removal above 75%). Long term process in static regime outlines the need for interim washing steps for avoiding clogging the catalytic surface and the same reasons recommends the process for highly diluted systems, as a tertiary step after the conventional wastewater treatment.

Key Words: thin film photocatalyst, photocorrosion, Vis photocatalysis

Acknowledgements: the authors thank the financial support of the UEFISCDI of the Romanian Ministry of Education and Research under the grant PN-IIPT-PCCA-2011-3.2-1235 (Contract No. 162/2012).

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O 39B – Miniaturised electrochemical sensors for environmental pollutant detection

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Abstract

Most of the toxic common pollutants such as heavy metals and pesticides are usually detected using analytical methods that require laboratory setup, such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry, gas chromatography, and high performance liquid chromatography. These techniques are characterized by complex instrumentation involving high costs and skilled personnel, which render them entirely unsuitable for “in field measurement”. In this context, efficient, sensitive, miniaturized, and cost-effective analytical tools has become extremely important for environmental control. Electroanalytical techniques coupled with screen-printed electrodes (SPEs) are acknowledged to be well suitable for pollutant detection. Furthermore, the high potentiality of SPEs lies in the possibility to fabricate “*ad hoc*” sensors, tailoring them with inorganic nanomaterials and/or biocomponent for the detection of several pollutants.

SPE modified with bismuth was coupled with a portable potentiostat for the simultaneous measurement of cadmium and lead ions by stripping analysis. The optimized analytical system allows the detection of both heavy metals at the ppb level (LOD equal to 0.3 and 2 ppb for lead and cadmium ions, respectively). The sensor was then successfully applied for the evaluation of Pb²⁺ or/and Cd²⁺ uptake by measuring the amount of the heavy metals both in growth medium and in plant tissues during 1 week experiments. In this way, the use of *Lemna minor* coupled with a portable electrochemical sensor allows the set up of a model system able both to remove the heavy metals and to measure “in-situ” the magnitude of heavy metal removal.

The potentiality of this type of sensors was also exploited for the detection of arsenic ions, pesticides and phosphate. In the first case, screen-printed electrodes were modified with carbon black (CBNPs) and gold nanoparticles (AuNPs). The As(III) was detected by CBNP-AuNPs/SPEs using anodic stripping voltammetry, with a high sensitivity and reaching a LOD of 0.4 ppb. Finally, CB-AuNPs/SPEs have been applied to As(III) trace analysis in drinking water, obtaining satisfactory recovery values (99±9%). The SPEs were also modified with Prussian Blue nanoparticles and a biocomponent like butyrylcholinesterase enzyme for pesticide detection. The detection of paraoxon (an organophosphorus pesticide) was carried out evaluating its inhibitory effect on BChE, and quantifying the enzymatic hydrolysis of butyrylthiocholine before and after the exposure of the biosensor to paraoxon, by measuring the thiocholine product at a working voltage of +200 mV. The biosensor was then embedded in a flow system for obtaining an automatable measurement reaching a detection limit of 1 ppb. The analytical system was then challenged in drinking, river and lake water samples. Matrix effect was minimized by using a dilution step (1:4 v/v) in flow analysis. The phosphate

detection is based on the monitoring of an electroactive complex obtained by the reaction between phosphate and molybdate that is consequently reduced at the electrode surface of SPE modified with CBNPs. Main analytical parameters of the automatable system such as working potential, reagent concentration, type of cell, and flow rate were evaluated and optimized. This system was characterized by a low detection limit (6 μM) and good recovery percentages, comprised between 89 and 131.5%, were achieved in different water sources.

Key Words: electrochemical sensor, screen-printed electrodes, heavy metals, organophosphorus pesticides, phosphate.

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O 40B – Characterization and application of Green Fenton-like catalysts for the removal of water pollutants

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Abstract

Purpose: Three types of magnetite-chitosan/iron oxalate/iron citrate nanoparticles (NP) were evaluated as magnetic heterogeneous catalysts for water treatment.

Experimental description: A modified facile procedure (chemical co-precipitation) for the synthesis of coated magnetic nanoparticles was employed, followed by a detailed characterization of the as-obtained nanocatalysts.

Results: The high-resolution SEM (Fig. 1) and TEM results revealed the morphology of primary nanoparticles with sizes ranging from 10 to 20 nm. The XRD analyses of the coated iron oxide particles showed the typical patterns for magnetite, while VSM measurements evidenced relatively high values of saturation magnetization of the catalysts. The catalytic activity in heterogeneous oxidation of aqueous solutions containing a model pollutant, Bisphenol A (BPA), was comparatively studied (Fig. 2).

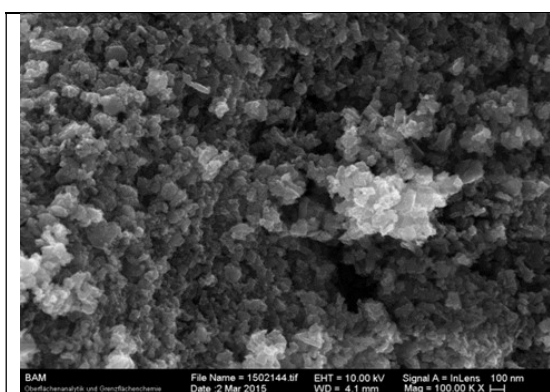


Fig. 1. SEM micrograph of the Fe₃O₄-chitosan/iron citrate nanocatalyst

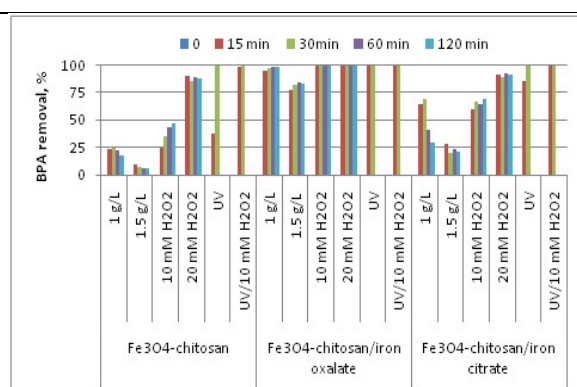


Fig. 2. The effect of catalyst loading, H₂O₂ dosage and UV light on BPA removal over three catalysts.

Conclusions: The effect of operational parameters (catalyst loading, H₂O₂ dosage and UV light) on the degradation performance of the oxidation process was investigated; the optimum experimental parameters were: 1 g/L of catalysts, 10 mM H₂O₂, under UV irradiation, for all catalysts and after 15 minutes of reaction, the micropollutant was completely removed over all catalysts. The highest mineralization rates were

observed for Fe₃O₄-chitosan/iron oxalate catalyst. The obtained results show that the catalysts are suitable candidates for the removal of persistent pollutants in wastewaters by means of the heterogeneous reaction.

Key Words: Bisphenol A, Fe₃O₄-chitosan/iron oxalate nanoparticles

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O 41B – Multivariate and geostatistical methods in urban soil geochemistry

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Abstract

Purpose: The aim of this study was to analyse soil concentrations of some potentially toxic elements (PTEs) in the southern Italy area of Cosenza and Rende municipalities in order to (i) define the pollutants baseline in soils, (ii) identify the most heavily polluted areas, (iii) assess the contributions of parent material and anthropogenic activity to geochemical baseline determining their different correlation structure to isolate sources of variation acting at different spatial scales. In addition, baseline data for urban areas of Cosenza and Rende can be used to assist policy makers and legislators to draw up a better legislation with more appropriate guideline/intervention values.

Experimental description: In the urban and peri-urban area of Cosenza-Rende, 149 topsoil samples were collected (0-10 cm) and analysed for 36 elements by XRF and ICP-MS. In addition, 18 samples of rocks were collected on outcrops of the whole area and analysed by ICP-ES and ICP-MS. MultiGaussian approach was used to map the concentrations of major oxides and several trace elements and principal component analysis and factorial kriging analysis were employed to identify the main factors influencing the PTEs spatial variability (Wackernagel, 2003).

Results: PTEs in soil samples showed a wide range of concentrations, primarily controlled by the geochemical composition of bedrock, with the notable exceptions of As, Pb, and Zn, whose concentrations are heavily affected by land use and anthropogenic pollution in urban areas (Guagliardi et al., 2012, 2015). Two groups of PTEs were identified: the first one included As, Pb and Zn; and the second one Al, Co, Cr, Fe, La, Nb, Ni, Ti and V. The first group was related to anthropogenic input, while the second one was more related to parent rock composition. The regionalized factors at different scales of variability allowed to aggregate and summarize the joint variability in the PTEs and consider the probable causes of soil pollution.

Conclusions: The geostatistical methods were the key role, which allowed us to identify PTE hot spots (those large enough to be identified at the sample density of the current survey) and areas that may pose potential risks to Cosenza and Rende inhabitants. Analysing and quantifying the sources of variation of PTEs acting at different spatial scale and defining the spatial anomalies based on the correlation structure associated at the different spatial scales, some anthropogenic and geogenic anomalous abundances are found in peri-urban areas. Finally, these results can be used to propose remedial actions aimed at reducing health risk above all to people.

References: **(1)** Guagliardi I., Cicchella D., De Rosa R., 2012. *A geostatistical approach to assess concentration and spatial distribution of heavy metals in urban soils*. Water Air Soil Poll, 223: 5983-5998. **(2)** Guagliardi I., Cicchella D., De Rosa R., Buttafuoco G., 2015. *Assessment of lead pollution in topsoils of a southern Italy area: analysis of urban and peri-urban environment*. J Environ Sci, 33: 179-187. **(3)** Wackernagel H., 2003. *Multivariate geostatistics: an introduction with applications*. Springer, Berlin.

Key Words: soil - potentially toxic elements - pollution - geostatistics

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O 42B – Fuel volatile compounds mobility in soils in the presence of plant root exudates

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Abstract

Purpose: Vegetation and its associated microorganisms play an important role in the behaviour of soil contaminants. One of the most important elements is root exudation, since it can affect the mobility, and therefore, the bioavailability of soil contaminants. In this study, we evaluated the influence of root exudates on the mobility of fuel derived compounds in contaminated soils.

Experimental description: Samples of humic acid, montmorillonite, and an A horizon from an alumi-umbric Cambisol were contaminated with volatile contaminants present in fuel: oxygenates (MTBE and ETBE) and monoaromatic compounds (benzene, toluene, ethylbenzene and xylene). Natural root exudates obtained from *Holcus lanatus* and *Cytisus striatus* and ten artificial exudates (components frequently found in natural exudates) were added to the samples, individually and as a mixture, to evaluate their effects on contaminant mobility. Fuel compounds were analyzed by headspace-gas chromatography-mass spectrometry.

Results: In general, the addition of natural and artificial exudates increased the mobility of all contaminants in humic acid. In A horizon and montmorillonite, natural or artificial exudates as a mixture decreased the contaminant mobility. However, artificial exudates individually had different effects: carboxylic components increased and phenolic components decreased the contaminant mobility.

Conclusions: The findings of this research could be useful for choosing the most appropriate phytoremediation species, according to the phytoremediation objectives (extraction, containment, immobilization or degradation). They also establish a base for developing and improving phytoremediation processes of fuel-contaminated soils.

Key Words: plant root exudates, BTEX and fuel oxygenates, contaminant mobility in soil

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O 43B – Environmental threat posed by endocrine disruptors in water bodies receiving sewage from major Polish cities and their WWTPs

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Abstract

One reason for increased incidence of various types of endocrine problems in hum beings are environmental pollutants particularly of anthropogenic origin. All human activities impact the environment, but some have significant strength, just to mention energy industry, mining, transportation, chemical, petrochemical or housing. Environmental stressors are a large group of compounds in terms of their physicochemical properties, some of which may disturb the biochemical processes taking place in the living organism causing, among others, genotoxic effects. Surface waters contaminated by urban and industrial effluents are becoming a wide reservoir of these compounds, and the current wastewater treatment technologies are not always able to meet this challenge.

Wastewater samples were collected in 2011-2013 from all the major sewage treatment plants of Poland. Next to all major and minor ions also ecotoxicity tests were conducted (Microtox® and Ostracodtoxkit F™) as well as Xenoscreen YES/YAS and comet assay. A good alternative to traditional analytical methods and immunotechniques or methods using living organisms as biomarkers of exposure to EDCs are cellular biotests. In this kind of tests, cells can be used unchanged or modified with proper bioengineering methods to obtain cells able to respond to the presence of EDC. The XenoScreen YES/YAS assay system can identify both activating (agonistic) and inhibitory (antagonistic) activities of samples tested. For the determination of antagonist activities, the samples are incubated in the presence of a fixed concentration of a reference agonist (17-β estradiol for YES and 5α-dihydrotestosterone for YAS). Inhibition of the response relative to this fixed agonist concentration is a sign of antagonist activity. The assay also identifies cytotoxic effects on the yeast cells.

Based on results of studies conducted it can be stated that:

acute toxicity could be observed in case of water samples collected in southern part of Poland where most of heavy industry and mining activities are located;

chronic toxicity could be observed in most cases of water samples collected after the treated waters release point;

endocrine potential was highly correlated to total organic carbon content and increased in almost all cases in water bodies receiving theoretically treated wastewaters,

studies on endocrine disruptors' effects enable monitoring of environmental degradation, determine threat posed by chemicals of EDC character and thus stating actions to prevent negative impact of EDCs on living organisms.

Key Words: endocrine disruptors, environmental risk assessment, WWTPs, biotests

Acknowledgements: The work has been financed by the Polish Ministry of Science and Higher Education grant no. IP2011 028071.

ShotGun Presentations

SG1 – Trace element profiling of hair in the neonate as a possible marker of maturity

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Abstract

Purpose: Determination of the trace element profiling of the hair in the neonate according to gestational age.

Experimental description: Trace element profiling using energy dispersion X-ray fluorescence technique in a sample of 80 neonates divided in groups according to gestational age.

Results: The composition of the studied elements in the analysed hairs was very similar between groups; the biggest difference observed between the control and the samples is the amount of aluminium. It was also verified that along each hair the concentration of most remains the same, i.e. their composition is about the same from root to tip. Regarding the analysed elements, sulphur as the highest relative concentration, ranging from 86-90%, followed by chlorine with 5-7% and calcium with 1-3%. The relative concentration of the remained studied elements is below 1% each. Furthermore, as the gestational age increase from group to group, the values of aluminium, iron, copper and zinc decrease and those of sulphur and phosphorus increase. On the other hand, chlorine, calcium and silicon, don't present apparent tendency for different gestational ages.

In terms of the total amount of trace elements, it was recorded for full-term, late preterm, very preterm and extreme preterm, the respective values of 20100 ± 2200 , 15300 ± 1800 , 12700 ± 1500 and 9600 ± 1400 mg/kg. The verified differences have weak evidence of significance. This can be attributed to the low volume of the samples and to other factors that may also contribute to the absorption of nutrients by the fetus besides the gestational age.

Besides the differences verified between groups there was ~~also~~ a substantial gap between them and the values obtained for the standard and adult sample, respectively, 64200 ± 2700 and 49100 ± 2600 mg/kg. These differences are very likely due to, again, the low volume of the samples and the heterogeneity of the hairs themselves. Finally, it's interesting to note that in some of the samples it was possible to observe the presence of iodine, signalling, most likely, some type of contamination at the time of labour.

Conclusions: The goal of the study was reached, as it was possible to analyse and differentiate the concentration of trace elements in different gestational age groups. During the study it was noticed that the data obtained is somewhat dependent on the volume analysed since the studied hairs were on the same scale

as the focal spot of the spectrometer. As such, the obtained values are affected by a systematic uncertainty. One possible solution could be using tablets made out of the analysed samples. However, considering that the donors are neonates, most of which preterm, it's highly doubtful that there would be enough hair samples in each donor to make a tablet and/or that the parents would give permission to remove such a considerable amount of their children's hair.

Key words: hair, neonate, ultrastructure, trace element, X-ray fluorescence.

Acknowledgments: This research was supported in part by the Rectory of Universidade Nova de Lisboa, "Determinação da concentração elementar de cabelos recém-nascidos termo e pré-termo". M.G. Acknowledge the support of the FCT, under Contract No. SFRH/BPD/92455/2013.

SG2 - Are biosurfactant and chelating agent mixtures good additives for electro-kinetic remediation of multi-contaminated sediments?

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Abstract

Purpose: This study focused on evaluating whether the biosurfactant (Rhamnolipid or Saponin) and chelating agent (Citric acid) mixtures are useful or not for electro-kinetic remediation of multi-contaminated sediments, which contain polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and also heavy metals. Another aim of this study was to reveal if a natural biodegradable biosurfactant could favorably replace synthetic surfactants to favor the organic decontamination of sediments.

Experimental description: The experimental electro-kinetic device consisted of a sediment chamber and two electrode compartments (applied voltage gradient: 1 V.cm^{-1}) filled respectively with two pumps for injecting the aqueous solutions of bio-surfactant and chelating agent mixtures. A reconstituted sediment was prepared by mixing different constituents (73% silt, 5% sand, 19.5% kaolinite, 2.5% organic matter) with an initial pH=8.5, mimicking the properties of a French dredged harbor sediment. Five PAHs (phenanthrene, fluoranthene, pyrene, chrysene and benzo(a)pyrene) and five PCBs (PCB 28, 52, 101, 138 and 180) were added to the dry sediment, which was aged for 4 months. A solution of 5 heavy metals (Cd, Cr, Cu, Pb and Zn) was mixed with the dry reconstituted sediment two days before the electro-kinetic remediation process started. Three tests were performed during 12 days, with a periodic voltage (5 days on, two days off): one run (1) using a mixture of rhamnolipid/citric acid as catholytes and anolytes, one run (2) without rhamnolipid in the cathode compartment and one run (3) using a mixture of saponin/citric acid in the two electrode compartments.

Results: This study showed that the non-ionic biosurfactant (saponin) and the anionic biosurfactant (rhamnolipid) gave almost the same capacity in remediating PAHs (approximately 25% decrease), which did not correspond to our previous researches. Indeed, non-ionic synthetic surfactants (such as Tweens) showed better results for PAH remediation, because they did not counteract the electro-osmotic flow (EOF) (from the anode to the cathode), which is not the case of anionic ones, that electro-migrate towards the anode. After each electro-kinetic treatment, the PAHs had a tendency of moving from the middle to the anode side when the Rhamnolipid and Saponin were used as additives, and so did the PCBs. But the remediation of PCBs was not significant, probably because of the too low concentration of bio-surfactants (1 g.L^{-1}). For heavy metals, the relatively best remediation was revealed when the Rhamnolipid was pumped only into the anode compartment (run n°2), compared to pumping the Rhamnolipid into both electrode compartments (run n°1). It means the ionic biosurfactant may not favor the remediation of heavy metals, probably because of its

adverse effect on EOF. The remediation results using Saponin mixed to citric acid (run n°3) was a little better than that with Rhamnolipid for Cd, Cr and Pb, but for Cu and Zn these two tests were similar. At last but not least, the benefit of the periodic voltage was not visible for this study (particularly on the current intensity), probably because the number of on/off cycles was too few.

Conclusions: These tests show that at the low concentration of Rhamnolipid/Saponin and Citric acid mixtures, the migration and elimination of multi-contaminants after the electro-kinetic remediation process was not significant, which need a higher concentration of bio-surfactants and chelating agent mixtures and also a longer treatment time.

Key Words: Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, heavy metals, bio-surfactant, chelating agent, electro-kinetic remediation

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Presented as poster P25

SG3 – Copper Removal by a smectite exchanged with cations (Na^{++} , Ca^{2+} et H^{+}) and intercalated by 3-aminopropyltriethoxysilane

Belhadri Mazouri

Abstract

The present study investigates the influence of the modification of Algerian clay on the capacity of copper removal from water. This clay has been saturated with sodium, calcium, treated with the acid sulphuric (10% and 20%) and intercalated by an oligosilsesquioxane by polymerization of monomer 3-aminopropyltriméthoxysilane. The adsorbants and metal interactions were studied under different conditions of interaction time, pH, concentration of metal ions and amount of clay. The interactions were dependent on pH and the uptake of pollutant was controlled by the amount of clay and the initial concentration of copper. The results of the kinetic study are described by a pseudo model of the second order and the isotherms of adsorption, followed by the equation of Longmuir. The results of this study showed that sodic clay has more affinity than the others adsorbants.

Keywords: smectite; pollution; pseudo order, Adsorption isotherm; copper, Langmuir and Freundlich model, diffusion.

SG4 – An efficient and eco-friendly approach for removal of chromium from the contaminated effluents by using a soil borne bacterium, *Enterobacter cloacae* B2-DHA

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Abstract

Purpose: Continued disposal of chromium and chromium containing compounds to the environment leads to development of various lethal diseases in both humans and animals. The purpose of this study was to identify, isolate and characterize naturally occurring bacterial strain(s) that can grow on chromium contaminated soil or water and can also accumulate chromium in the cells thus reducing the level of this toxic metal in the contaminated source to a safe level.

Experimental description: The bacterial strain B2-DHA was isolated from a landfill containing effluents disposed from leather manufacturing tannery industries in Bangladesh. In this study we have used several modern techniques to localize chromium in the bacterial cells qualitatively and quantitatively. Dynamic time of flight secondary ion mass spectrometry (TOF-SIMS) imaging and depth profiling have been employed to follow the distribution of chromium ion and its products within the cells. Inductively coupled plasma - mass spectrometry (ICP-MS) has been used to measure the amount of chromium in the dry bacterial cells. The concentration of chromium in the cell free broth has been measured by using the inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

Results: B2-DHA has been proven to be resistant to chromium with a MIC value of 1000 µg/mL potassium chromate. TOF-SIMS and ICP-MS analyses confirmed intracellular accumulation of chromium. Chromium accumulation in cells was 320 µg/g of cells dry biomass after 120 h exposure and thus it reduced the chromium concentration in the liquid medium by as much as 81%. Environmental scanning electron micrograph (ESEM) revealed the effect of metals on cellular morphology of the isolates.

Conclusions: Our results confirm that B2-DHA has the potential to reduce chromium significantly to safe levels from the contaminated environments and suggest the potential use of this bacterium in reducing human exposure to chromium, hence avoiding poisoning. Consequently, the findings will contribute to a significant positive impact on the socio-economic status of the people particularly in the affected regions.

Keywords: Bioremediation, chromium, *Enterobacter cloacae*, human health, tannery effluents, soil borne bacterium

Acknowledgements: This research has been funded by the Swedish International Development Cooperation Agency (SIDA, grant no. AKT-2010-018), the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS, grant no. 229-2007-217) and the Nilsson-Ehle (The Royal Physiographic Society in Lund) foundation in Sweden.

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SG5 – Second raw materials from forestry waste to obtain adsorbents for wastewater treatment

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Abstract

Purpose: Of the total water on the surface only 1% meets the standard of consumption, such 1.2 billion people haven't access to drinking water. Continuous development has resulted in large amounts of wastewater. The demands for water for industrial and human consumption are increasing.

We must find new methods of wastewater treatment. One of the solutions for solving these problems would be use of forest residues for obtaining new adsorbents. These are forestry waste residues, resinous cones processed into charcoal. Most of the dyes are organic compounds, with different degree of polarization, making their complete biodegradation slow or even impossible. Adsorption on charcoal obtained from forestry waste residues represents a possible alternative for removal of dyes and heavy metals from wastewaters resulted in the textile industry. The paper the results obtained in the simultaneous removal of heavy metal and dye, using a powder of charcoal.

Experimental description: Using charcoal powder from resinous waste in different condition, comparative studies of the adsorption mechanisms are presented; the experiments are reported considering two types of wastewaters containing: (1) heavy metal cations (cadmium), and (2) dye (Methylene blue) and single heavy metal.

An amount of 2g mixed substrates, was dispersed in 100 mL of solution containing the pollutant(s). Two series of tests were done, on solutions containing: (1) CdCl₂, (99.9%, Scharlau); (2) CdCl₂ with Methylene blue (MB, C₁₆H₁₈ClN₃S, Merck).

The optimal contact time was evaluated based on the efficiency - time graphic correlations. Using the optimized adsorption parameters, the adsorption isotherms were experimentally obtained for cadmium concentrations up to 0.01 mg/L and for dyes concentrations up to 0.05mmol. The initial and equilibrium cadmium concentrations were measured using atomic absorption spectroscopy (**AAS Zeenit, Analytic Jena, at $\lambda=228.8$ nm**). **The dyes concentration was calculated based on uv-vis spectroscopy** (Perkin-Elmer Lambda 25 spectrometer), on the calibration curve, at the maximum experimental absorption wavelength ($\lambda_{MB}=665$ nm).

Results: The results proved that a 30 min contact time of the substrate with the pollutant(s) solution is enough to reach good removal efficiencies, and this was set as optimal value. Adsorption tests were done on substrates, varying the charcoal amount. The results show that this substrate has a good affinity for MB, as

result of the rather large amount of carbon and for cadmium (that can be explained due to the surface charge) also.

The dye in the mixture has as consequence an increase in the substrate capacity for cadmium adsorption, and a complexation mechanism of the metal ion with the adsorbed MB is likely.

The experimental adsorption isotherms for cadmium and MB, are described by the Langmuir isotherm for cadmium adsorption from mono-ionic solutions and from solutions also containing MB.

Conclusions: The charcoal obtained from forestry waste can be efficient substrate for a single step wastewater treatment process, in the dye finishing industry. The results proved that charcoal are able to remove, with efficiencies above 90%, both dye (MB) and heavy metal (cadmium).

Keywords: forestry waste, adsorption, wastewater treatment.

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SG6 – Heavy metals and methylene blue removal from wastewater by zeolite synthesized from fly ash

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Abstract

Purpose: The goal of this paper was to develop zeolites from fly ash by hydrothermal treatment modified with NaOH used for advanced wastewater treatment, for removal of one dye – methylene blue (MB) and heavy metals – Cd^{2+} , Cu^{2+} , Ni^{2+} from synthetic wastewaters containing one, two, three and four pollutants.

Experimental description: Class “F” fly ash (FA) used for synthesis of the two zeolites (ZCET FUS and ZCET AL) was collected from the electro – filters from Central Heat and Power Plant Brasov, Romania. The oxides composition $\text{SiO}_2/\text{Al}_2\text{O}_3$ over 2.4 makes it a viable precursor for zeolite synthesis.

The two zeolites were obtained from modified fly ash with NaOH by hydrothermal treatment, both of the materials were obtained under the same conditions the difference between them was that ZCET AL was obtained by adding $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ during the treatment. These materials were further used in adsorption experiments. The parameters that were optimized for obtaining maximum efficiency during the adsorption process were: contact time and optimum amount of substrate. The optimized parameters were used in thermodynamic and kinetic studies of the adsorption processes.

Results: The obtained materials were characterized using XRD and SEM. The XRD data show that in the zeolites composition new crystalline phases like sodium aluminum silicate hydrate (phillipsite) ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$) appear. The SEM images show a compact and regular structure.

The surface of the materials is negatively charged and because of this all the pollutants were removed with good efficiencies. From the heavy metals the Cu^{2+} is hydrated in aqueous solution with 4 molecules of water, unlike 6 for Cd^{2+} and Ni^{2+} , because of this the best removal efficiency was obtained for Cu^{2+} .

During adsorption processes from systems containing MB and heavy metals, the efficiency for removal of heavy metals is bigger because MB acts as a complexing agent which increases the affinity of heavy metals.

Conclusions: The results show that the new materials can be used for obtaining adsorbents that can be further used in advanced wastewater treatment. The tested substrates in adsorption processes proved good efficiencies for removal of MB and heavy metals from the synthetic pollutant systems. The best efficiencies were obtained for the removal of MB and Cu^{2+} . The contact time was set at 60 minutes because it was considered optimal and it is technologically feasible. The kinetic studies indicate that the adsorption of all the four pollutants follows the pseudo-second order equation.

Key Words: fly ash, hydrothermal treatment, methylene blue, heavy metals, zeolite, adsorption.

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SG7 - Colorimetric studies on the interaction with ions using two urea-containing compounds

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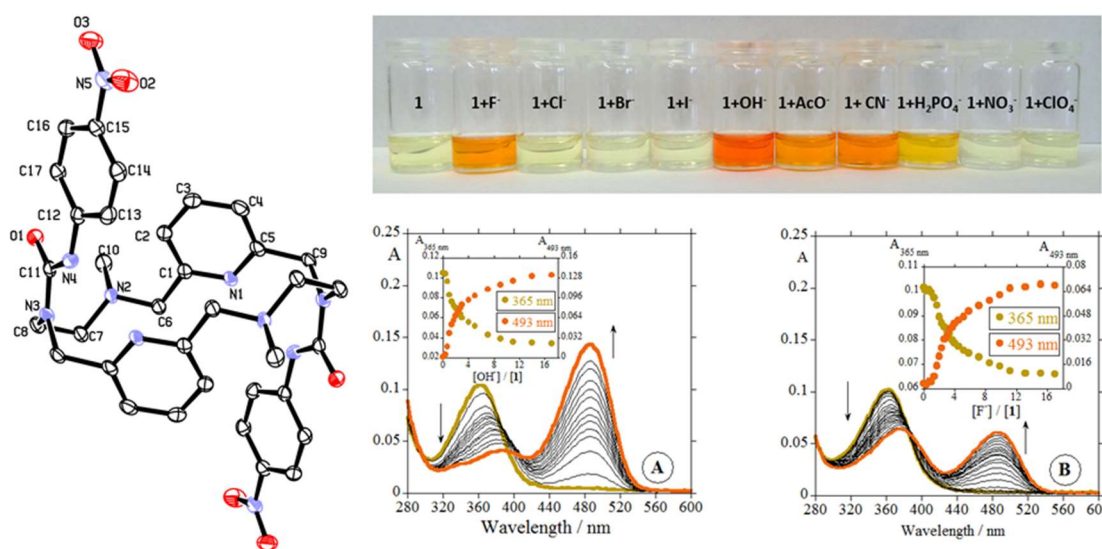
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Abstract

Purpose: The principal aim of this work was to explore the potentiality to use two novel *trans*-substituted molecular probes in the presence of different toxic anions as colorimetric sensors.



Spectroscopic results with 1 in the presence of OH⁻ and F⁻

Experimental description: The interaction of systems 1 and 2 with different anions (F⁻, Cl⁻, Br⁻, I⁻, OH⁻, CH₃COO⁻, CN⁻, H₂PO₄⁻, NO₃⁻ and ClO₄⁻) was explored by spectrophotometric titrations in DMSO.

Results Different reactions were observed upon the addition of the anions. They show a colorimetric response with the addition of the more basic ones, such as OH⁻ and F⁻, changing the colour from pale yellow to orange. Moreover, just compound 1 show a colour change with the addition of H₂PO₄⁻.

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SG8 - Metabolic response of the clam *Scrobicularia plana* under arsenic exposure

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Abstract

Purpose: In this study the potential toxicity of arsenic present in water, generally as As(V), on aquatic living organisms such as the clam *Scrobicularia plana*, a bivalve very frequent at the southwest coast of Spain and Portugal has been assessed, due to the ability of this mollusk to transform metabolically the As (V) toxic in other less toxic chemical species, as monomethyl (MMA) and dimethylarsenic (DMA), or innocuous ones as arsenobetaine (AB). Correlatively, other important metabolic changes are triggered by the presence of arsenic, such as enzymatic inhibition, impaired antioxidants metabolism and oxidative stress, which determines the still unclear mechanisms of arsenic toxicity^{1,2} that remains still unclear.

Experimental description: The clam *Scrobicularia plana* was exposed to 10 and 100 $\mu\text{g}\cdot\text{L}^{-1}$ As(V) during 14 days and the metabolic response compared against a control. 50 mg of digestive gland was submitted to a double extraction (MeOH:H₂O 80:20 and Cl₃CH:MeOH 2:1) to obtain polar and non-polar extracts. On these extracts were performed As speciation (AEC-ICP-ORS-MS) and metabolomic studies based on direct infusion mass spectrometry (DI-ESI-QqQ-TOF-MS). Results were statistically treated by multivariate analysis (PLS-DA), and the metabolites with significant influence in the classification of exposed and control samples were identified by MS/MS experiments and data base assessment.

Results: The metabolomic study allows a good classification of samples associated to low and high As(V) exposure in relation to controls. About 15 metabolites suffer significant changes of expression by the presence of As(V): amino acids, nucleotides, energy-related metabolites, free fatty acids, phospholipids and triacylglycerides, which can be related to membrane structural and functional damage related to toxicological action of inorganic arsenic and perturbation of methylation cycle, associated to the increase of homocysteine and methionine that enhance the methylation of toxic inorganic arsenic to less toxic dimethylarsenic.

Conclusions: Metallomic and metabolomic approaches allow to deep insight into the characterization of metabolome changes introduced by As(V) exposure in living organisms, such as is the case of clam *Scrobicularia plana*. Perturbation of cell membrane stability, energy cycle and methylation has been observed. This analytical approach contributes to the knowledge of arsenic toxicity in aquatic environments and its consequences.

Key Words: Arsenic toxicity, arsenic speciation, metabolomics, metallomics, arsenic exposute

Acknowledgements: This work was supported by the projects CTM2012-38720-C03-01 from the Spanish Ministry of Economy and Competitiveness and P12-FQM-0442 from the Regional Ministry of Economy, Innovation, Science and Employment (Andalusian Government, Spain). Gema Rodriguez-Moro thanks the Ministerio de Economía y Competitividad for a predoctoral scholarship (Grant nº BES-2013-064501).

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SG9 – Use of Electrical Leaching as an experimental analogy for nuclear decay in ILW

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Abstract

Purpose: The aim of this set of research was to examine if it is possible to use electrical leaching as an analogy to nuclear decay in intermediate level waste (ILW)- specifically, to make a simulated cementitious wasteform and then use electrical leaching to pull in barium in the form of $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$. This was done to examine if such experiments are possible and how such an experiment affects the cement matrix, and is in theory similar to the chloride diffusion test employed in the civil engineering industry. Cs-137 is a problematic radionuclide in ILW due to its mobility and abundance with a half-life of 30 years. The end of its decay chain is Ba-137, and electrical leaching provides us with a unique opportunity to examine how a cement matrix behaves when Ba is electrically migrated into it after hydration has already occurred.

Experimental description: As it is used in the UK to encapsulate ILW, 3:1 Blast Furnace Slag:Portland Cement (3:1 BFS:PC) tile-shaped samples were produced (40 x 40 x 5 mm) and $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$ was dissolved into the water used to hydrate the cement (0.34 w/b). Cement formulation: 600g BFS, 200g PC, 15.232g $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$, 272g distilled H_2O . The amount of $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$ was chosen for its solubility limit. The sample is placed in the center of the migration cell with 750ml of distilled water in both tanks, and 0.32g of $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$ was dissolved into the anode tank's water to match the average moles of $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$ in each sample. The samples were then leached with a current density across the sample of 25 Am^{-2} for 3, 7 and 14 days. Samples with $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$ and no additions were also produced and leached, with (3, 7, 14 days) and without (28 days) electrical current applied.

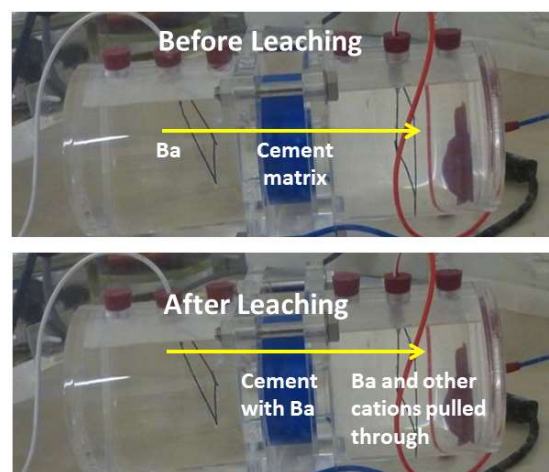


Figure 1 Experimental setup. Anions are attracted to the anode and cations to the cathode

Results: XRD shows that Barite (BaSO_4) is formed when the cement is made with $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$, and seems to not be affected by e-leaching when compared with the control test, suggesting that this mineral is immobilized in the cement matrix. Importantly, this phase is also seen when $\text{Ba}(\text{OH})_2 \cdot 8(\text{H}_2\text{O})$ is dissolved into the anode solution used for leaching a 'blank' 3:1 BFS:PC sample, suggesting that the Ba can react with the matrix and forms Barite after the cement matrix has already become hydrated.

Conclusions: Barite forms when Barium is electrically leached into a 3:1 BFS:PC matrix, suggesting that it will also form when Cs-137 decays into Ba-137 in ILW. This is important as Cs is highly mobile in the wastefrom and can move in a flowing water environment, but Barite is highly immobile and so and Cs that becomes Ba and forms Barite due to the presence of Sulphur in the cement matrix will become immobilized.

Key Words: Nuclear Waste, Nuclear Decay, Cement, Electrical Leaching, Barium

Acknowledgements: The cement samples were produced in the University of Sheffield and all experiments conducted at the Lifetime Engineering Laboratory, Hokkaido University with Dr. Katsufumi Hashimoto as part of a three month secondment. Thanks goes to the EPSRC for funding, the Nuclear FiRST DTC, the University of Sheffield and Hokkaido University.

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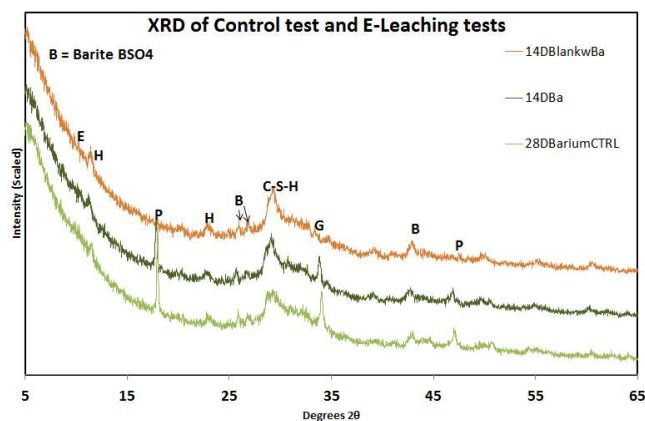


Figure 2 Selection of XRD data showing formation of Barite

Poster Presentations

P1 – Multiple-solvent hollow fiber liquid phase microextraction (MSS HF-LPME) for simultaneous determination of semivolatile DBP in drinking water

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Abstract

Purpose: Disinfected water has been shown to contain Haloacetic acids (HAAs) and Trihalomethanes (THMs), but there is evidence to suggest that significantly more than 600 chemical DBPs may also exist (Richardson, 1998). There is considerable uncertainty over the identity and levels of DBPs that can affect the population through drinking water. Since most studies have focused on THMs and HAAs analysis, there is a need for comprehensive quantitative occurrence and toxicity data to determine whether other DBPs have present and represent health risk (Richardson et al., 2003). In this study, a novel multiple-solvent simultaneous microextraction method has been performed and applied to pre-concentrate semi-volatile species of DBPs including Iodo-trihalomethanes (I-THMs), Haloacetonitriles (**HANs**), Haloaldehydes (Has), Haloketones (**HKs**), Halonitromethanes (**HNMs**). This procedure was performed in one step by using two different solvents (immiscible with each other) supported in two filter membranes (1 cm × 1 cm), which were used as extraction devices.

Experimental description: A method based on liquid hollow fiber membrane microextraction (HF-LPME) and GC- μ ECD for analysis was developed. The method is simple, reproducible and cheap; reaching low detection limits that makes the approach suitable for routine laboratories control in water distribution systems. The method was applied for the determination supply water samples from water distribution systems in the Huelva area, located at the southwest Spain, which use different water-treatment processes.

Results: The analytical performance of the optimized procedure was evaluated and good linearity, reproducibility and accuracy were obtained together to low detection and quantification limits. The method allows fast extraction and high pre-concentration of analytes, reduction of organic solvent, elimination of carry-over effects using disposable fibers and high applicability to different water matrices

Key Words: multiple-solvent, Hollow fiber membrane, Gas chromatography, Disinfection by-products, Drinking water.

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P2 – Presence of organochloride pesticides and PCBs in the andalusian serum population for the epidemiological evaluation of the environmental pollution

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Abstract

Purpose: Organochloride contaminants (organochloride pesticides and PCBs), and other persistent organic pollutants (POPs) are widely spread in the environment as a consequence of their wide use in industrial and agricultural activities. Therefore, they can get the population especially due their lipophilicity that provoke their accumulation in different organs of human, causing important harmful effects such as immunodeficiency, neurological dysfunctions, reproductive disorders, and hormonal changes. Then, the evaluation of the presence of POPs in the population allows assessing the environmental risk that they suffer. For this purpose non-invasive sampling procedures using fluid easy to obtain from human as is the serum have been used for epidemiological assessment of POPs in the Andalusian region in the south Spain.

Experimental description: About 600 serum samples from the eight Andalusian provinces were sampled during March to September 2015. Aliquots (3 mL) of spiked blank serum were equilibrated for 3 h at medium temperature (18 °C) and pollutants were extracted with methanol and n-hexane–dichloromethane (3:1, v/v; 5 mL). The organic extract was dried under a gentle stream of nitrogen. Sample was added to 100 µL of hexane. POPs were analyzed by GC-ECD and GC-MS. A total of 27 organochloride pesticides and 21 PCBs were analyzed.

Results and Conclusions: the concentration of these POPs was established and statistical comparison between their presences in the different Andalusian provinces has been performed. Conclusions about the environmental risk of Andalusian population and health consequences have been established.

Key Words: organochloride pesticides, PCBs, Andalusian population risk, GC-MS

Acknowledgements: This work was supported by the projects CTM2012-38720-C03-01 from the Spanish Ministry of Economy and Competitiveness and P12-FQM-0442 from the Regional Ministry of Economy, Innovation, Science and Employment (Andalusian Government, Spain).

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P3 - Theoretical and experimental approach of the $\text{Zr}_{1-x}\text{Hf}_x\text{SiO}_4$ study: A stable matrix for radioactive waste immobilization

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Abstract

ZrSiO_4 and HfSiO_4 are of considerable interest because of their low thermal expansions, thermal conductivities, and the optical properties of HfSiO_4 . In addition, silicate phases of both are studied as radioactive waste disposal materials. ZrSiO_4 - HfSiO_4 exhibits ideal condition to form a solid solution, as predicted by first principles calculations. However, only the structure of ZrSiO_4 doped with Hf 1% has been published. Therefore, the aim of this work was to shed a light on the solubility and cation distribution of the ZrSiO_4 - HfSiO_4 system thorough under a theoretical and experimental point of view.

$\text{Zr}_{1-x}\text{Hf}_x\text{SiO}_4$ ($x=0, 0.25, 0.5, 0.75$ and 1.0) were synthesized by intimately mixing stoichiometric amounts of oxides and heated at 1823 K for 20 days in a platinum crucible. The solids were characterized by XRD (Rietveld analysis) and ^{29}Si MAS NMR. Finally, first principles phase diagram calculation was performed using density functional theory (DFT).

XRD and first principle calculations have demonstrated the formation of a solid solution in all range of composition but with a negative deviation of the Vegard's law (Figure 1 a-b) which should be explained by the partial cation ordering observed by ^{29}Si MAS NMR (Figure 1c).

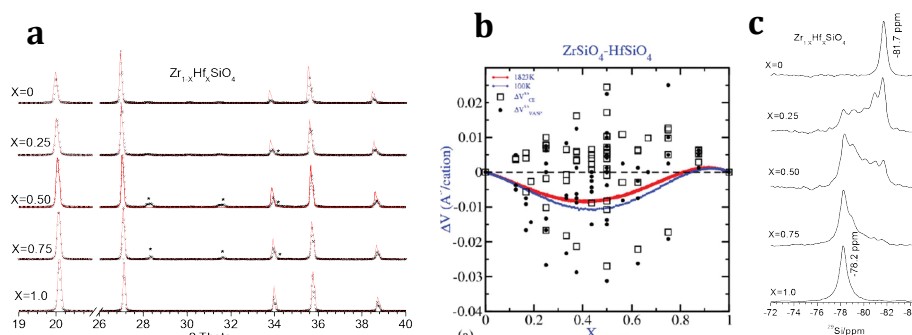


Figure 1. a) XRD patterns of $\text{Zr}_{1-x}\text{Hf}_x\text{SiO}_4$. b) Plot of molar volume CE (CE_v) fitted to DFT-calculated molar volumes, and the calculated theoretical trend: solid circles indicate DFT values for V/cation ; open squares indicate CE_v calculated values; near-continuous curves (blue and red) indicate $V(X)$ trends for calculated cation distributions at 1823K and 100K, respectively. c) ^{29}Si MAS NMR spectra of $\text{Zr}_{1-x}\text{Hf}_x\text{SiO}_4$

Key Words: ceramic, radioactive waste, phase diagram

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P4 – *Callitriche cophocarpa* proteome under chromate stress

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Abstract

Purpose: to analyze protein patterns obtained for *Callitriche cophocarpa* Sendtn. (water starwort, a widespread macrophyte) upon incubation with sublethal chromate concentrations. The plant reveals unusual response to chromate stress and is a potent Cr bioremediator and hyperaccumulator. Cr(VI) occurs in the environment as a highly hazardous anthropogenic pollutant with a strong oxidizing activity. It enters cells *via* anion transporters and then causes severe damage upon reduction to lower oxidation states. Chromate is a source of physiological, especially oxidative, stress reactions which result in altered proteomic profiles. Using 2D-electrophoresis, comparative proteomic analyses were performed to identify both the Cr(VI)-induced and suppressed proteins. The differentiating protein spots were excised from gels and subjected to identification by a MS/MS-based microsequencing. The aim was to verify whether the changed protein profiles result from a specific chromate action or they rather non-specifically reveal some similarities with other stressful conditions such as salt, temperature, and oxidative stresses obtained with paraquat and hydrogen peroxide.

Experimental description: *C. cophocarpa* was treated for 72-h with 1mM potassium chromate in a Murashige-Skoog (MS) medium at 25°C. Other physiological stress conditions were as follows: (i) salt stress: 24-h incubation with 150mM NaCl, then 48 h at control conditions (MS medium, 25 °C); (ii) temperature stress: 24-h incubation at 33°C, then 48 h at control conditions; (iii) oxidative stress: 5 min incubation with paraquat or hydrogen peroxide, then 72 h at control conditions. After treatments, the protein content was extracted and mapped with 2-DE using IPG strips of the pI range 3-10 and 5-8, and then compared with the respective control profiles (lack of stress conditions). All the electrophoretic runs were performed in triplicates.

Results: *C. cophocarpa* reacted to the applied physiological stress by changing proteomic profiles. For the salt and temperature stresses the observed alterations were minor as compared to Cr(VI) treatment. For the latter case, the most pronounced changes involved the following polypeptides: (1) induction of a protein of molecular mass M=21.7 kDa, pI=6.3; (2) induction of M=20.8 kDa, pI=7.3; (3) down regulation of M=50.1 kDa, pI 6.7; (4) suppression of M=35.9 kDa, pI=7.6; (5) suppression of M=29.8 kDa, pI= 7.7. Microsequencing was followed by bioinformatic analysis using NCBI databases confined to *Viridiplantae*. Mascot peptide ion scores served as bases for ranking protein hits. The most important result is the high-ranked identification of a protein of the spot (1), *i.e.* flavin mononucleotide-binding, NAD(P)H-dependent quinone dehydrogenase (FQR1 of *Vitis vinifera*) which is known as an enzyme responsive to oxidative stress and exhibits *in vitro* quinone reductase activity. Neither temperature nor salt stresses caused any such result whereas the patterns obtained with paraquat and H₂O₂ suggest that this protein might be induced by oxidative stress.

Conclusions: *Callitriche cophocarpha* treated with chromate reveals significant changes in proteomic patterns which resemble the response to oxidative stress factors and are different from other stress conditions. Cr(VI) possibly induces the expression of a quinone reductase that catalyzes the transfer of electrons from NAD(P)H to several substrates. This activity is expected to be a detoxification enzyme, possibly protecting the cells against oxidative stress and is not induced by other stress conditions such as the salt and temperature stresses.

Key Words: macrophyte, *Callitriche*, chromate, bioremediation, oxidative stress

Acknowledgements: The work was financially supported by the research grant of the Polish National Science Centre no. DEC-2011/03/B/NZ9/00952. Microsequencing was done at the Institute of Biochemistry and Biophysics of the Polish Academy of Sciences, Warsaw, Poland

P5 – Determination of sugar-beet herbicides and their metabolites in surface and ground water in an area of Valladolid (Spain)

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Abstract

Purpose: A survey of herbicides and their metabolites present in surface and ground waters were conducted during two years in an area of the province of Valladolid (central-western of Spain) to assess the degree of pollution of the agricultural area and changes in time due to the presence of herbicide and metabolite residues.

Experimental description: Ten sites of ground and surface waters were sampled for the simultaneous determination of phenmedipham, ethofumesate, metamitron and three of their degradation products; m-toluidine, 2-aminophenol and metamitron-desamino. A previously optimised method involving preconcentration of samples by solid-phase extraction with a strong cation exchange phase (SampliQ C8/Si-SCX Mixed Mode) provided the best results in the enrichment of 200 ml of water. Optimization of the elution step showed that the best results were obtained with 2,5 ml x2 of methanol and ammonium hydroxide. The analysis was performed by means of HPLC-ESI-MS. Recovery studies showed that the evaporation of the eluted is a critical step of the extraction procedure, because some volatile compounds can be partially lost during evaporation. Good recoveries were obtained in ultrapure water when samples were spiked at 0.1 and 1 µg/L as required by the Drinking Water Directive 98/83/CE. When environmental waters were used a matrix effect was observed and therefore a matrix-matched calibration was used.

Results: Regarding to the active substances, in surface waters, few samples showed residues of phenmedipham and ethofumesate up to 6 µg/L and 0.3 µg/L respectively. As for metabolites, 2-aminophenol was not detected and the most detected compound was toluidine (a metabolite of phenmedipham) with a highest concentration of 7 µg/L. Regarding groundwater analysis, few samples showed residues of the active substances. Phenmedipham and ethofumesate were detected up to 0.5 µg/L at times far after the application that could be due to leaching processes. As for the metabolites, only toluidine was detected at a concentration level above the permitted limit of 0,1 ppb.

Conclusions: The results reveal a possible relationship between water pollution and time of application of herbicides. In surface water, detections of active substances occur at the moment of application and afterwards there is an absence of residues. However, in ground water residues of active substance appear far from the application season. In all the samples analyzed, metabolite toluidine is by far the most detected compound. To sum up, we can conclude that not only the active substance but also their metabolites are important to be monitored, which can be present at levels above the legal permitted level.

Key Words: sugar-beet herbicides, metabolites, LC/MS, ground and surface waters

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P6 - Development of SPE-LC-MS/MS methodology to the assessment of pharmaceuticals in treated water samples from wastewater treatment plants

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Abstract

Purpose: Recently, thanks to new and more sensitive equipments has been possible the detection of other potentially harmful pollutants, called emerging contaminants. Due to this fact and the increasing of their use, the interest in having information about their presence in the environment is considerably growing [1]. In this work, we optimised Solid Phase Extraction (SPE) technique and the parameters of Liquid Chromatography tandem Mass Spectrometry (LC-MS/MS) for the extraction, detection and quantification of seven pharmaceutical compounds, including caffeine (stimulant), nicotine (stimulant), atenolol (beta blocker), metamizole (anti-inflammatory and analgesic), fluoxetine (antidepressant), paraxanthine (stimulant) and clofibric acid (lipid regulator), which belong to different therapeutic classes. The optimised methodology was applied to evaluate the presence of these pharmaceutical compounds in treated water samples from Wastewater Treatment Plants (WWTPs) of the Gran Canaria island (Spain) during a year.

Experimental description: All parameters involved in SPE were optimised, such as, type of SPE cartridge, sample volume, pH and ionic strength of sample, desorption volume and wash step. The results were evaluated using a Liquid Chromatography system with Diode-Array Detector (LC-DAD) and C₁₈ column to obtain optimum extraction conditions with lesser cost. Moreover, the optimisation of the LC-MS/MS parameters, such as fragment ion, cone voltage and collision gas energy, was carried out to improve the analysis response and detection. All analytical parameters (LOD, LOQ, repeatability and accuracy) were determined in order to validate the proposed analytical method. SPE extraction combined with LC-MS/MS was applied to the monitoring of wastewaters from three different WWTPs located on the island of Gran Canaria.

Results: Application of the developed method to the analysis of treated wastewaters from three different wastewater treatment plants of the island of Gran Canaria indicates the presence of most of the compounds under study. The concentrations were in the range of 0.02–12.31 µg L⁻¹.

Conclusions: The proposed method (SPE-LC-MS/MS) for the evaluation of seven pharmaceutical compounds in treated wastewaters is sensitive, robust, reproducible, simple, and applicable to real samples. It is also a method that can be applied in laboratories that routinely analyse a large number of samples per day. The detection limits that were achieved with the method were appropriate for the detection of pharmaceuticals in real samples.

Key Words: Pharmaceuticals, SPE, LC-MS/MS, wastewater

Acknowledgements: C. Afonso thanks to FPU Grant Program of the Spanish Ministry of Education and Science.

Reference: [1] C. Afonso-Olivares, Z. Sosa-Ferrera, J.J. Santana Rodríguez. Journal of Environmental Science and Health, Part A (2012) 47, 887–895.

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P7 – Arsenic-Induced Oxidative Stress in Barley (*Hordeum vulgare*)

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Abstract

Purpose: In this study, physiological parameters of Balkan 96 species of barley (*Hordeum vulgare*) of Arsenic (As) such as germination rate, root length and dry and wet weight were evaluated in 10 μ M (low and non-toxic dose) and 50 μ M (high and toxic dose) two concentrations, its effect on antioxidative enzymes such as superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APx), Guaiacol peroxidase (GPx) in root tissue of arsenic and effect on lipid peroxidation which is an important determinant of oxidative stress were evaluated, the effect of barley on arsenic toxicity was analyzed in biochemical sense.

Experimental description: We tested the effects of arsenate (10 and 50 μ M) on seed germination, and on relative root and shoot length, soluble total protein contents, and malondialdehyde content in barley roots. All biochemical analyses were performed at 4 C; 0.2 g of roots were extracted in 2ml of 50 mmol/l K-phosphate buffer (pH 7.0) including 1.0 mmol/l EDTA and 0.01% (w/v) polyvinylpyrrolidone. The homogenate was centrifuged at 15000 rpm for 30 min, and the supernatant was used for the enzymatic assays. The activity of superoxide dismutase (SOD) was assayed based on its ability to inhibit NBT photochemical reduction (Beuchamp and Fridovich 1971). The activity of Ascorbate peroxidase (APx) was determined by measuring the decrease in absorbance at 290 nm ($\epsilon=2.8 \text{ mM}^{-1}$) due to oxidation of ascorbic acid to dehydroascorbate (Nakano and Asada 1981). Guaiacol peroxidase (GPx) activity was determined by the increase in absorbance at 470nm due to guaiacol oxidation. ($\epsilon=26.6 \text{ mMcm}^{-1}$). Catalase (CAT) activity was measured as the disappearance rate of H_2O_2 at 240 nm. ($\epsilon=39.4 \text{ mM}^{-1}\text{cm}^{-1}$). Protein amounts were spectrometrically measured according to Lowry method (Lowry et al. 1951). The thiobarbituric acid (TBA) method was used to measure MDA content, which is indicative of lipid peroxidation, in root tissues (Sun et al. 2008). Seed germination percentages of As treated seeds were calculated relative to that of the control.

Results: Relative root and shoot length, and seed germination decreased with increasing concentrations of arsenate. In general, the protein content in roots decreased with increasing doses of As. Besides, against oxidative stress caused by arsenic, barley reacted in root tissue with changes in antioxidative enzyme activities such as superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APx), Guaiacol peroxidase (GPx). While there was a significant ($p<0.005$) decrease in activities of APx and CAT enzyme activities, there was increase in SOD enzyme activities. There was no significant change in GPx enzyme activity.

Conclusions: In conclusion, barley seedlings subjected to As treatments showed oxidative stress symptoms, such as an increase in lipid peroxidation. In addition, As treatments resulted in a decrease in α -amylase activity, and changes in the reducing sugars contents and total protein contents. These biochemical changes affected the plants and inhibited their growth, depending on the As dose. These data show that barley plants can use various defense mechanisms to protect themselves against As, up to a certain critical concentration.

Key Words: Arsenic, Barley (*Hordeum vulgare*), Lipid peroxidation , Antioxidative Enzymes

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P8 – Morphometric analyses of leaves *Betula pendula* and *Corylus avellana* at Malachov Hg-waste heap (Western Carpathians, Slovakia)

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Abstract

Purpose: The aim of study was to determine the differences in morphometric traits of the most frequency pioneer deciduous trees species *Betula pendula* and *Corylus avellana* on the Hg-waste heap Malachov (Central Slovakia) with higher contents of heavy metals in soil and on non-toxic reference site (RS). The anticipated differences would be demonstrated the impact of heavy metals from mining heap on plants through which get into the food chain.

Experimental description: The field research was realized in September 2014. We focused on width and length of leaf blade and length of petiole. On both sites we marked 20 individuals by stratified selection. We measured 500 leaves on every tree (after 5 leaves at 5 branches). The results were subjected of statistical analysis using a Student *t*-test, indicators of variability and central values.

Results:

<i>Betula pendula</i>						
Central values	Leaf blade width		Leaf blade length		Petiole length	
	heap	RS	heap	RS	heap	RS
Measurements	500	500	500	500	500	500
Average	3,921	5,982	4,909	7,068	1,571	1,892
Median	3,8	5,9	4,8	7	1,6	1,9
Variance	0,799	1,819	0,973	1,636	0,058	0,085
Standard deviation	0,895	1,350	0,987	1,280	0,240	0,292
Coefficient of variation	0,223	0,226	0,201	0,181	0,153	0,154
<i>t</i> -test (significant level)	0 (99 %)		0 (99 %)		0 (99 %)	

We confirmed very similar results with *Corylus avellana*.

Conclusions: Variability of measured characteristics of both species shows their high morphological plasticity on habitats. Influence of heavy metals was significantly reflected on deviations in all morphometric features, when the leaves of individuals on heap were markedly smaller (in average around 1/3 smaller) what we can evaluated as dwarfism. The same time we observed necrosis and chlorosis of leaves, formation a smaller number of trunks of *Corylus avellana*, overall lower growth and subsequently slower total height. Further research we want focus on determine the bioaccumulation characteristics of both pioneer species usable in the process of phytoremediation.

Key Words: heavy metals, heap, contamination, dwarfism, *Betula pendula*, *Corylus avellana*, Slovakia

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P9 – Use of the Landfill Water Pollution Index (LWPI) for groundwater quality assessment near the landfill sites

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Abstract

Purpose: The purpose of the paper is to assess the groundwater quality near the landfill sites using Landfill Water Pollution Index (LWPI).

Experimental description: To investigate the scale of the groundwater contamination a three landfills, in different phase of its exploitation (new, old and closed landfill) were taken for analysis. A samples of groundwater in surrounding of analyzed landfills were taken four times a year since 2004 till 2014. A total of over 400 groundwater samples were analyzed for pH, EC, PAH, TOC, Cr, Hg, Zn, Pb, Cd, Cu, which are - which are required by UE legal acts for landfill monitoring system. To each of the analyzed parameter were assigned weights values, reflecting the influence of each parameter on groundwater quality.

Results: The calculated value of the LWPI allowed the quantification the overall water quality near the landfill sites. Conducted analyses revealed that the LWPI can be used for evaluation the degree of water pollution near the landfill, for assessment the variability of results with time and for comparison the results obtained from different places and time periods.

Conclusions: The applied WQI can be also an important information tool for the landfill policy makers and public about the groundwater pollution threat from landfill.

Key Words: groundwater quality, landfill impact, pollution, water quality index

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P10 – Detecting Al (III) using a Synthetic Gold Nano-antibiotics sensor

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Abstract

Purpose: Aluminum is one of the most abundant metal ions in the earth, and is well known to be a neurotoxic environmental agent. This metal may be involved in certain diseases such as Alzheimer or Parkinson among others, hence is urgent the necessity to detect and remove selectively this metal in contaminated waters. Continuing with our scientific interest in synthesis and application of noble metal nanomaterial as chemical sensor, we have designed a new aqueous one-pot synthesis of gold nanoparticles functionalized with the antibiotic tetracycline (AuNPs@TC).

Experimental description: AuNPs@TC was obtained using tetracycline molecule as reducing and stabilizing agent in basic aqueous medium under temperature stimulation. The AuNPs@TC were analyzed using UV-vis spectroscopy, FT-IR, DLS and Transmission Electron Microscopy (TEM and HRTEM).

Results: The pink colloidal system obtained presents a SPR band at ca. 530 nm having an average size of 26+/-5 nm showed (Figure 1). Our AuNPs@TC can detect colorimetrically 300 nM of Al(III) inducing a color change from pink to blue as a result of interaction with Al (III) which produce aggregation in the colloidal system. The reversibility of this colorimetric reaction was explored adding EDTA to the solution of AuNPs@TC in the presence of Al(III). Complexation between the EDTA with the aluminium(III), releasing the tetracycline stabilized nanoparticles, and restoring the original pink color of the colloidal system.

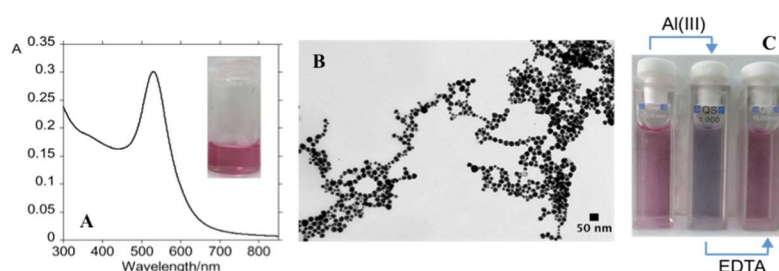


Figure 1. UV/Vis spectra and colour solution (A), TEM images (B) and change colour solution in presence of Al(III) and extraction with EDTA. (C)

Conclusions: The synthesized AuNPs@TC permits the uses of these AuNPs as a colorimetric selective chemosensor for Al(III) in water. The reversibility observed permits to use this system as recover the sensor upon removing the Al(III) of environmental water.

Key Words: gold nanoparticles, tetracycline, aluminum, chemosensors

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P11 - Exploration of genes involved in the aerobic dechlorination of Hexachlorobenzene in *Nocardioides* sp. PD653

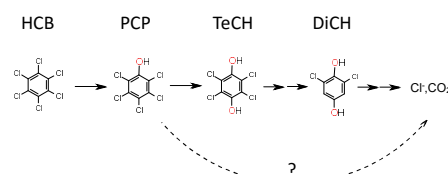
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Abstract

Purpose: Hexachlorobenzene (C_6Cl_6 ; HCB) is an organochlorine fungicide which has been used worldwide since 1940s. *Nocardioides* sp. PD653 is the first bacteria capable of mineralizing HCB under aerobic conditions¹. The putative metabolic pathway of HCB in strain

PD653 was proposed in Fig.1. HCB is mineralized via Pentachlorophenol (PCP). Various bacterium was found to degrade PCP, and the genes has been elucidated in detail in *Shingobium chlorophenolicum* ATCC 39723². We assume that this pathway is contributed to degradation of HCB in the same manner. However, dehalogenase involved in initial step of aerobic dechlorination of HCB is still unknown. Therefore, the aim of this study is isolation and identification genes which are involved in dechlorination of HCB.



[Fig.1] Possible metabolic pathway of HCB by strain

Experimental description: Bacterial strain and genomic DNA. Strain PD653 and PD653-B2 lacking activity for dechlorination of HCB to PCP were incubated in culture medium for 3 d. Total DNA was purified using a DNeasy Blood and Tissue kit (Qiagen) according to the manufacturer's instructions. Draft genome sequencing. A library of sequencing was prepared by a NEBNext DNA library prep master mix set for Illumina (New England Biolabs, Ipswich, MA, USA) and pair-end sequenced (2 x 300 bp) on a MiSeq sequencer using a MiSeq version 3 reagent kit (Illumina KK, Tokyo, Japan). The genome was annotated by the NCBI Prokaryotic Genome Annotation Pipeline (PGAP version 2.8). The distribution of related genes. The distribution of genes encoding redox proteins predicted as HCB degradation protein was compared between strain PD653 and PD653-B2 genomes using GENETYX ver.12.

Results: The draft genome sequence of strain PD653 and PD653-B2 were performed using the MiSeq platform and read assembly yielded 5.08 Mb (87 contigs) and 4.99 Mb (81 contigs), respectively. As a candidate gene for the metabolism of HCB, flavin-dependent oxidoreductase was postulated because deletion or modification of this gene was found. We confirmed whether this gene was deleted or modified in strain PD653-B2 by PCR. Strain PD653 had this gene, but not detected in strain PD653-B2.

Conclusions: It is suggested that flavin-dependent oxidoreductases might be responsible for dechlorination of HCB to PCP. We are conducting cloning and expression of this gene in *E.coli*.

Key Words: Hexachlorobenzene, persistent organic pollutants, aerobic dechlorination, draft genome sequencing

Acknowledgements: This work was supported by a cooperative research grant from the Genome Research for BioResource NODAI Genome Research Center, Tokyo University of Agriculture.

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P12 – Leaching potential of fuel volatile compounds from contaminated soils using closed-column and TCLP leaching tests. Influence of plant root exudation

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Abstract

Purpose: Fuel volatile compounds such as fuel oxygenates (FO) (MTBE and ETBE) and BTEX (benzene, toluene, ethylbenzene and xylene) are some of the most soluble components of fuel. Characterizing their leaching potential appears essential to predict their mobility through the soil profile to groundwater and to evaluate the associated risks. Root exudates can play an important role in the modification of contaminant mobility in the soil-plant system, and its effect should be also carefully studied.

Experimental description: For this purpose we used artificially spiked samples of A and B horizons from an alumi-umbric Cambisol. These samples were leached in closed-columns and TCLP batch experiments using Milli-Q water and a plant root exudate solution extracted from *Holcus lanatus*.

Results: The results indicated that the leaching potential and rate was highly influenced by the interaction between the sample and the contaminants, and by the presence of root exudates. Organic matter in A horizon preferably sorbed the most apolar contaminants, lowering their leaching potential, and this was enhanced by the presence of root exudates. On the other hand, the inorganic components of the B horizon, showed higher affinity for polar molecules, and root exudates provoked an increase in contaminant desorption. Column experiments resulted in a more realistic protocol to predict the leaching potential of volatile organics in dissimilar soils.

Conclusions: These experiments provide reliable data on fuel volatile compounds leachabilities based on contaminant-soil-root exudates interactions, which can be used for contaminant dynamics modeling in the soil system and for selecting the suitable soil remediation technique and avoid the contamination of groundwater. These procedures also provide useful data to be used in risk assessment of contaminated soils, and their potential pollution of wells and aquifers.

Key Words: leaching potential; fuel volatile contaminants; root exudates; TCLP; packed closed-columns

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P13 – Sentinel Parasite - The Existence and Relevancy in the Environments

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Abstract

Purpose: To examine metal pollution and parasites association on the notion of complex environments.

Experimental description: Endoparasites were examined from different hosts that are specific to each group of interest. The assessment of the studied organism in terms of growth, evaluation of the uptake or toxicity of the metal(s), and the environmental parameters (i.e. pH) were taken into account to aid in quantification of bioavailability of each parasite.

Results: Groups of Acanthocephala, Cestodes, Digenea and Nematoda from fresh water samples showed positive accumulation of As, Al, Ag, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Mg, Mn, Ni, Pb, Sb, Sn, Sr, Tl, V, and Zn with the ratio of metal concentration in parasite tissues to metal concentration in the host ranging from 0.2 – 600.

Conclusions: Water acts as a major source of heavy metal pollution, thus, reflects the existence of sentinel parasites. From this study, parasites served as bio-indicators of heavy metal contamination. Hence, the findings are crucial to discover and explore other parasites in human host that may potentially be used as an alternative in determining contamination obtained from water sources.

Key Words: Heavy metal, Endoparasites and Environment

Acknowledgements: This study was supported by UMRG 544/14HTM and UMRG 362/15AFR.

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P14 – New emissive pseudo-crown compounds bearing amino acids as lateral side chains: From chemosensors to Nanoparticle design

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Abstract

Purpose: Crown ethers have a strong affinity and high selectivity for alkali and alkaline earth metal ions, because of the nature of their binding sites and to the presence of a hydrophilic cavity. Their complexing properties by cations and anions have applications in many areas. Herein, two new bio-inspired chemosensors incorporating cysteine residues, **L1** and **L2**, containing sulphur atoms such as cysteine or methionine were synthesized and their sensing ability studied towards alkali, alkali-earth, transition and post-transition metal ions.

Experimental description: The synthesis of compounds L1 and L2 were performed by HOBt/DCC coupling reaction with protected cysteine in DMF solution. The final products were purified by chromatography column gel. Photophysical characterization of L1 and L2 was realized in CH₂Cl₂ solution (ca. 10⁻⁵ M). Titrations were carried out by the addition of small amounts of standard solutions of alkali, alkali-earth, transition and post-transition metal ions in dry acetonitrile (ca. 10⁻³ M).

Results: The compounds show an absorption and emission bands at 290 nm and 330 nm, respectively, being

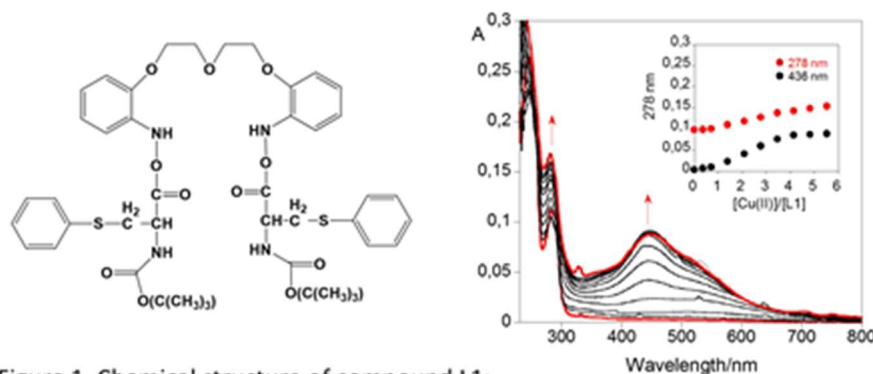


Figure 1. Chemical structure of compound L1; Spectrophotometric titration with addition Cu²⁺ metal ions in dichloromethane.

practically no emissive, with fluorescence quantum yield of $\Phi < 10^{-3}$. Among all metal ions added, such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺, Cu²⁺, Pb²⁺ and Hg²⁺, the most pronounced changes were verified with Cu²⁺ whereas a new band at

450 nm (d-d transitions) was observed.

Conclusions: A selective and Colorimetric probes for Cu²⁺ metal ions were successful obtained.

Key Words: Chemosensors, Nanoparticles, Zinc(II), Copper (II), Mercury (II).

Acknowledgements: E.O., H.M.S acknowledges the post-doctoral grant from Fundação para a Ciência e a Tecnologia (FCT-MEC) (Portugal) SFRH/BPD/72557/2010 and SFRH/BPD/73997/2010, respectively. Authors also thank PROTEOMASS Scientific Society (Portugal), UCIBIO: UID/Multi/04378/2013 and REQUIMTE-FCT PEst-C/EQB/LA0006/2013 for general funding.

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P15 – Presence of toxic forms of arsenic in rice. Differential accumulation in paddy and husked rice

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Abstract

Purpose: Food and water are the most important source of arsenic exposure to human¹. The estimated human intake for this element is in the range 12 to 20 µg of As per day. Inorganic forms of arsenic (As(III) and As(V)) are more toxic and toxicity decreases in organic species, being methylated arsenic (MMA and DMA) considered as moderately toxic^{2,3}. Therefore, is important to know the arsenic species present in food products, especially in rice and its products, in which it has been demonstrated, recently, the presence of significant amounts inorganic arsenic^{4,5}. In the present study an analytical approach for arsenic speciation has been optimized and applied to different types of rice paddy and husked to check the presence of inorganic and organic arsenic in the food and the differential accumulation in rice grain and husk.

Experimental description: It has been developed a speciation method for As based on previous reports from Francesconi et al⁷ using a soft extraction with trifluoroacetic acid (TFA) followed by the analysis of (As (III), As (V), DMA y MMA) by anion exchange liquid chromatography and detection by ICP-MS. This procedure has been checked using a certified reference material containing all these species (IRMM-804).

Results and Conclusions: A total of 129 samples of rice were analyzed by the optimized speciation procedure. The results show that As (III) and DMA are the most abundant arsenic species in rice samples, especially in paddy rice. On the other hand, MMA and As (V) are absent in husked rice, which denotes the migration of these species to rice husk. This fact is very important due to the higher toxicity of As (V).

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Key Words: arsenic speciation, paddy rice, husked rice

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P16 – Long-term biostabilization of xenobiotic-degrading microbial consortia

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Abstract

Purpose: The main aim of the research was to elaborate the most efficient procedure of a long-term storage of microbial communities specialized at biodegradation of organic pollutants with the use of variant sample preparation techniques and several cryoprotectants.

Experimental description: The tests were carried out using a ZB-01 specialized microbial consortium earlier constructed by our group, consisting of environmental strains isolated from sites contaminated with petroleum-derived products. ZB-01 proved capable of efficient biotransformation of a number of hydrocarbon xenobiotics and has been used for cleanup of polluted areas. Samples of ZB-01 harvested at the late log-phase (cell density of 10^9 colony forming units (CFU)/ml) were subjected within years 2003-05 to a long-term storage. 0.5 ml aliquots were biostabilized with the use of cryoprotectants: trehalose (18 samples), sucrose (9), glycerol (5) and dimethylsulphoxide (DMSO, 5), applied at variant preincubation times (15 min to 4h). Next, the samples were prepared for storage either by direct freezing at -20°C , rapid freezing with liquid N, or freeze-drying, and then were kept frozen at -20°C till 2015. Respective controls were stored in the absence of any protective substance. After storage, unfrozen samples were reanimated either directly by plating onto solid optimal medium (enriched agar) and counting CFUs after 72h or by inoculating into optimal SNB medium in 25-ml flasks and rotary-shaking for 24h. Microbial frequency and biodiversity were tested with a Koch plating technique and colony morphotype evaluation. Metabolic activity of the consortia against xenobiotics (petroleum oil, hexadecane, decane or naphtalene) was estimated with a dehydrogenase assay (14-d) using triphenyltetrazolium chloride (TTC). The most active samples were also tested in a direct kinetic 7-d test of 1% decane biodegradation capability employing gas chromatography analyses. Freshly cultured ZB-01 consortium served as a reference biocenosis for evaluation of the biochemical potential of the long-term stored degraders.

Results: In a direct plating test 13 of the stored microbial suspensions formed colonies: 7 were stabilized with trehalose, and 6 with sucrose. Upon 24-h incubation in a SNB liquid medium, 11 samples showed intense growth: 5 stabilized with sucrose, then DMSO (3), trehalose (2) and glycerol (1). None of the control samples (lack of cryoprotectants) were able to proliferate. The number of the observed morphotypes varied from 2 to 8, and bacterial frequency after growth in liquid cultures ranged 10^4 to 10^{13} CFU/ml. The TTC assay proved strong metabolic activity for most of the tested samples incubated with different xenobiotics. The samples that showed the highest decane biodegradation capabilities were subjected to decane biotransformation tests after inoculation into erlenmayer flasks and treatment with this hydrocarbon. Two samples stabilized with trehalose, and two with sucrose, showed good, almost 100% biodegradation of the tested xenobiotic within 7 days.

Conclusions: The microbial ZB-01 consortium mixed with sucrose and trehalose added as cryoprotectants showed good preservation effects under long-term freezing conditions, especially when the samples were freeze-dried prior to storage. The reanimated consortia kept relatively high biodiversity and proved able to metabolize aliphatic and aromatic xenobiotics and efficiently biodegrade decane. The degradation kinetics were close to the ones obtained for the case of the freshly grown ZB-01 biocenosis. DMSO and glycerol appear as relatively poor cryoprotectants, resulting in lower survival and reduced activity of the tested consortium.

Key Words: cryoprotectants, sucrose, trehalose, consortium, lyophilization

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P17 - Impact of mining on environment at Malachov Hg-deposit (Western Carpathians, Slovakia)

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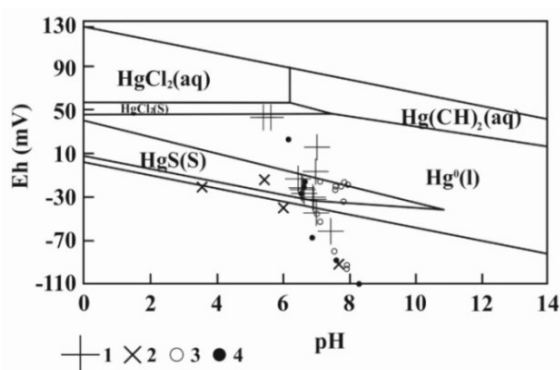
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Abstract

Purpose: The closed Hg-deposit Malachov in Central Slovakia belongs to the most important historic Hg deposits of Europe. The main aim of the presented study was to determine the Hg- As- and Sb-contamination in country components (soil, technosoil from the dumps, groundwater and surface water, plants, fauna).

Experimental description: The Hg content in soil, stream sediment samples and plant samples was determined by automatical spectrometer AMA 254. The Hg, As and Sb contents in water were analyzed by hydride generation atomic absorption spectroscopy. Hg, As and Sb speciation was determined using pH-Eh diagrams (Davis et al., 1997, Filella et al, 2002; Pokrovski et al., 2002; Ryu et al., 2002).

Results: The highest Hg concentrations in soil (44.24 mg·kg⁻¹) were described from the area of the last mining activity. Mercury contents are 0 – 403 µg·L⁻¹ in surface water and 0 – 0.99 µg·L⁻¹ in groundwater. The Sb and As contents in surface water are below detection limit, whereas, in groundwater, the Sb content ranges from 0.92 µg·L⁻¹ to 1.99 µg·L⁻¹ and As content in range <1 – 1.99 µg·L⁻¹. The stream sediments in the Malachovský brook contain Hg in the form of HgS. The Hg speciation both in soil and in water show presence



of Hg²⁺ (in the form of HgS) and, rarely, also of Hg⁰ (fig. 1), As and Sb are mainly present both in the soil/dump sediments and in the water in the very toxic As³⁺ and Sb³⁺ form.

Fig. 1 Stability fields for solid and liquid species of Hg using pH/Eh plot according to Davis et al. (1997); Explanation: 1 – soil/technosoil, 2 – stream sediment, 3 – surface water, 4 – groundwater

Conclusions: Mercury is generally of low mobility because of its high density and of its resistant sulphide compounds so the Hg release to the environment is limited. In the substantial part of samples, mercury is present in sulphide form, rarely also in form of elementary Hg⁰. No indication of methyl-mercury formation was found. The differences in the Hg/Fe, Hg/As and As/Sb correlations between soil and technosoil reflect presence of mineralogical associations as well as the results of the sorption of above mentioned metals on natural sorbents. The As and Sb speciation proved in all samples predominantly occurrence of the three-valent forms of As³⁺ and Sb³⁺. Intensive weathering of soil does not accelerate Hg bioavailability in a significant way because of its not very reactive sulphide form.

Key Words: mercury, contamination, soil, water, speciation

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P18 - Fast metabolomics approach for lung cancer diagnosis in environmentally polluted areas. The case of Huelva province (Spain)

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Abstract

Purpose: Epidemiology studies confirm the high occurrence of lung cancer in Huelva province which can be associated to mining and industrial activities¹. Because of the high mortality associated with this disease and the low survival ratio after his diagnosis, the development of rapid methods for early diagnosis of the disease is of great interest.

Experimental description: A metabolomic approach based on DI-ESI-QTOF-MS of serum samples, after sample pretreatment with organic solvents for protein precipitation, has been applied to compare the metabolic profile of patients with lung cancer, non-cancer lung disease and healthy ones, in order to elucidate the possible metabolic changes caused by lung diseases, as well as those caused by cancer. A total of 40 serum samples, 14 from lung cancer patients, 14 lung disease patients (LD) and 12 healthy controls (HC) have been analyzed and results statistically treated by partial least square discriminant analysis (PLS-DA).

Results: Twenty one altered metabolites were identified in lung cancer comparing them with healthy volunteers (urea, L-Thr, L-Orn, L-Gln, 3 LPL, 10 PL, and 4 TGs). On the other hand, twenty seven perturbed metabolites were identified in lung cancer compared to other lung disease patients (urea, L-Thr, L-Gln, C14-CAR, phosphocholine, 2 LPL, 16 PL, and 4 TGs). The major altered metabolic pathway in lung cancer was the glycerophospholipid metabolism, although the behavior of phospholipids in lung cancer was different when compared with healthy controls and non-cancer lung disease patients. The presence of phospholipids increases in LC with respect HC, but decreasing in LC respect to LD.

Conclusions: DI-ESI-QTOF-MS provides a fast approach for profiling and identification of metabolites related with LC, with a very wide coverage of metabolites avoiding the drawbacks associated to the chromatographic filter present in the couplings HPLC-MS and GC-MS. This fact increases the potential of this technique for the identification of biomarkers related to fast lung cancer diagnosis.

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Key Words: lung cancer diagnosis, direct infusion mass spectrometry, serum, Huelva lung cancer occurrence

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Innovation, Science and Employment (Andalusian Government, Spain). Grant 125/2012 from Spanish Society of Pneumology and Thoracic Surgery- SEPAR and Grant 8/2012 from South Association of Pneumology and Thoracic Surgery- NEMOSUR. Belén Callejón-Leblic thanks the Ministerio de Educación, Cultura y Deporte for a predoctoral scholarship, grant nº FPU13/03615.

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P19 – Toxicity study of DDE on mice *Mus musculus* under exposure experiments using environmental metabolomics

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Abstract

Purpose: The presence of DDE and others organochloride compounds have important environmental consequences due to endocrine disruptor nature of these compounds. To know the biological response of free-living animals to these pollutants exposure experiments of model organisms will provide information of the metabolic changes induced by these compounds, and, in this sense, the application of omics techniques, such as metabolomics, represents a good approximation^{1,2}. On the other hand, selenium is well known for its detoxification properties. Therefore, additional exposure experiments combining toxic (DDE) and non-toxic (Se) compounds have been performed in order to check the protective effect of this essential element on pollution episodes.

Experimental description: Exposure experiment of *Mus spretus* mice to DDE in the presence and absence of Se has been performed. A double metabolomics platform based on the complementary use of DI-QqQ-ESI-TOF-MS and GC-MS for the analysis of *Mus spretus* liver extracts has been developed. Subsequently the data were processed by multivariate statistical analysis to identify the metabolites altered in the exposure.

Results: Alterations of various metabolic pathways, such as energy metabolism (glycolysis, Krebs cycle), lipid metabolism (free fatty acids), amino acid metabolism (glutamine, aspartic acid, ornithine, etc) and oxidative stress (inosine), have been observed along exposure to DDE. Moreover, the presence of selenium shows a protective effect in these metabolic changes

Conclusions: Metabolomics based on the use of DE-ESI-QqQ-TOF and statistical analysis is a powerful tool to assess the mode of action of environmental pollutants as DDE. At the same time, some substances as selenium counteracts the toxic mechanism of this pollutant and has a significant detoxifying action in these episodes.

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Key Words: DDE, exposure experiments, *Mus musculus*, environmental metabolomics, selenium

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P20 – Biodegradation of hydroxylated PCBs by *Sphingomonas* sp. strain N-9 isolated from forest soil

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Abstract

Purpose: It has been reported that PCBs have been converted to hydroxylated PCBs (OH-PCBs) through variety mechanisms, including metabolic transformation in living organisms or abiotic reactions with hydroxyl radicals. OH-PCBs may have higher toxicity than PCBs as their parent compounds, because OH-PCBs had high degree of aqueous solubility. However, only a few reports have been published describing the bacteria degradation of OH-PCBs. The aims of the present study are to isolate the bacteria which can degrade OH-PCBs, and to investigate the degradation capacity of OH-PCBs. OH-PCBs may convert into products increased toxicity by biodegradation. Thus, we evaluated the toxicity of OH-PCBs metabolites after incubation with strain N-9.

Experimental description: Strain N-9 was basically cultured in mineral medium with yeast extract 0.05% and 4OH-3 chlorobiphenyl (CB). Concentrations of nine types of OH-PCBs and their metabolites of OH-PCBs were analyzed by an UPLC-MS (Waters, Milford, Massachusetts, USA) with InertSustain Phenyl HP Colum. PC12 cells (the cell lines derived from a pheochromocytoma of the rat adrenal medulla) were used to examine the cytotoxicity of OH-PCBs (4OH-3CB and 4OH-3,5CB) and their metabolites [4OH-3chlorobenzoic acid (CBA) and 4OH-3,5CBA]. Cell membrane damage was detected by a lactate dehydrogenase (LDH) assay, and cell shapes were observed by a microscope.

Results: We isolated *Sphingomonas* sp. strain N-9 from forest soil using mineral medium with 4OH-3CB. The concentration of 4OH-3CB (10 mg/L) was decreased in inverse proportion to growth and covered to 4-Hydroxy-3 chlorobenzoic acid (4OH-3CBA) for 1 day cultivation. Efficiencies of degradations of OH-PCBs by strain N-9 were depended on positional relationships between hydroxyl groups and chlorinates on rings. For examples, 100% of 4OH-3CB was transformed, while 4OH-2CB and 4OH-4'CB was transformed 32.8±0.2% and 23.0±1.5%, respectively. Strain N-9 utilized lowly chlorinated OH-PCBs which have 1-4Cl. In the toxicity evaluations, 4OH-3CB and 4OH-3,5CB induced cell membrane damage (LDH release), and caused a dose-dependent increase in neuron elongation of PC12. On the other hand, 4OH-3CBA and 4OH-3,5CBA did not induce cell membrane damages and neuron elongation. These results indicate that 4OH-3CB and 4OH-3,5CB can be lowered toxicity by strain N-9 which decomposed to CBA.

Conclusions: We succeeded in isolation of *Sphingomonas* sp. strain N-9 which degrades OH-PCBs with 1-4Cl. Our results suggest that strain N-9 transforms OH-PCBs to CBAs which have lower toxicity.

Key Words: OH-PCBs, Biodegradation, *Sphingomonas*, toxicity evaluation, PC12

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P21 – Biodegradation of melamine in aged soil by three melamine-degrading bacteria

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Abstract

Purpose: The aim of this study was to investigate the ability of *Althrobacter* sp. strain MCO and strain CSP (from upland soil)¹⁾, and *Nocardioides* sp. ATD6 (from paddy soil)²⁾ to degrade melamine in aged upland soil.

Experimental description: All strains were pre-incubated with R2A broth or melamine liquid culture. The pre-culture samples were adjusted to OD₆₀₀= 1.0 with PB. The soil sample was collected from upland field (0-20cm) that had received treatments of lime nitrogen including melamine in the eastern part of Japan. 77g wet soil (= about 50g dry weight) was set in 200 ml jar. Each 2ml culture sample was inoculated in soil, and thoroughly mixed. All samples were incubated at 25°C in the dark. Moisture adjustment and soil mixing were conducted every 5 days, and melamine in soil was measured every 10 days for 30 days. The method of melamine extraction was according to heat-alkali with ultrasonic extraction method and the melamine was measured by HPLC-UV. As stimulation test to inoculated strains, we also investigated addition of activation material to the aged soil.

Results: Using R2A broth as pre-culture, *Althrobacter* sp. MCO could finally degrade 54% of melamine during 30 days of incubation, but *Althrobacter* sp. CSP and *Nocardioides* sp. ATD6 could hardly degrade melamine (approx. 25%). The addition of activation material in soil enhanced the degradation of melamine by each strain, and they could degrade over 50% of melamine after 30 days incubation. Especially, strain MCO could degrade 72% of melamine after 30 days incubation, and the degradation rate was the best score in this study. Changed the pre-culture from R2A broth to melamine liquid medium, the degradation rate of melamine in soil was also remarkably increased, and all strains could degrade over 50% of melamine after 30 days incubation.

Conclusions: Although strain MCO and CSP were isolated from same upland soil, there is a clear difference of degradation rate in aged soil. We demonstrated that using melamine liquid pre-culture or addition of activity material resulted in improvement of melamine-degradation ability even in strain CSP and ATD6 which showed low degradation ability in aged soil. From this research, it is important for biodegradation in aged soil to maintain degrading activity against melamine. Moreover, the findings indicate that already reported degrading bacteria which could not degrade in aged soil such as strain CSP or were isolated from different soil type such as strain ATD6, might be possible to enhance their degradation ability.

Key Words: Melamine, Bioaugmentation, *Arthrobacter* spp., *Nocardioides* sp., Biostimulation, Aged soil

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P22 – A new analytical approach for the accurate screening of chlorophenols in water samples

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Abstract

Purpose: Disinfection is the most important process in the treatment of drinking water supply and is the final barrier against pathogenic bacteria and viruses before its distribution to consumers. However, water disinfection with chlorine and chloramines results in the formation of disinfection by-products (DBPs), which are of potential human health concern. Chlorophenols, are a group of emerging DBPs, which have recently caused significant concerns because their carcinogenicity. Indeed, these pollutants are considered generally much more carcinogens than the currently regulated ones. Thus, knowledge on the occurrence of these compounds in drinking water is important for sanitary and future regulatory purposes. So, the main objective of this study was to develop a fast, simple and highly sensitive analytical methodology for the determination of ultra-trace levels of trichlorophenol and pentachlorophenol in water samples. It combines solid-phase extraction (SPE) with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC/MS/MS).

Experimental description: Extraction and analytical conditions were optimized for trichlorophenol and pentachlorophenol in different water samples. Both SPE procedure, using Oasis hydrophilic-lipophilic balanced (HLB) cartridges (200 mg) and UPLC/MS/MS technique were investigated. Chromatographic separation was performed using an Acquity UPLC C18 column and a mobile phase consisting of acetonitrile, water, and formic acid (60: 40: 0.1, v/v/v) at a flow rate of 0.4 mL/min. Quality control analysis based on recovery studies, blank analysis, determination of limits of detection and precision was also performed in order to investigate the performance of the proposed analytical method.

Results: The run time of the developed instrumental method was four minutes. The performance of the proposed analytical procedure was studied in terms of linear calibration curves, linearity ($r^2 \geq 0.998$), precision ($<4.4\%$) and accuracy (between 99% and 102%). Using the SPE and UPLC/MS/MS, the target compounds were satisfactorily recovered (77-124%) and very low limits of detection were obtained (between 0.04-0.80 ng/L). Moreover, the calculated matrix effect was within 97-104% at all quality control levels.

Conclusions: The results showed that the developed method is simple, highly sensitive and accurate for the simultaneous determination of chlorophenols at traces levels in different types of water samples. The excellent performance of the developed method, as well as the short analysis time makes it a promising analytical tool for the screening of chlorophenols in aqueous samples. The target compounds were detected in very low levels and only in very few of the analyzed water samples. This clearly indicates the good quality

of drinking waters and the effectiveness of the protection measures adopted in France. None of the water samples analyzed exceeded the maximum legislated levels in the European Union.

Key Words: trichlorophenol, pentachlorophenol, drinking water, solid-phase extraction, ultra-performance liquid chromatography

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P23 – Impact of smoke exposure on the onset and evolution of lung cancer. A metabolomic approach

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Abstract

Purpose: The great occurrence of lung cancer over the world and the serious consequences of its onset¹ have promoted new analytical approaches providing integrated information about the metabolic changes caused by this disease onset and evolution, which could be used for early diagnosis of the disease. In this context, it is important to consider the influence of smoking exposure, defined as cigarette pack-years (P/Y), on metabolic profiles and metabolomics is a useful tool for this purpose.

Experimental description: A total of 21 patients were included in the study: (a) 9 healthy non-smokers controls; (b) 6 LC patients (4 Adenocarcinomas, 1 Squamous Cell Carcinoma, 1 Large Cell Carcinoma) with moderate P/Y (<35); and (c) 6 LC patients (2 Adenocarcinomas, 3 Squamous Cell Carcinoma, 1 Small Cell Carcinoma) with high P/Y (>70). Metabolites were analyzed by direct infusion into a high-resolution mass spectrometer (DI-ESI-QTOF-MS). The metabolic profiles obtained were subjected to multivariate statistical analysis (PCA and PLS-DA).

Results: The 3 groups under study showed marked differences between metabolic profiles, which allowed for the identification of potential biomarkers. Glutathione levels were decreased in serum samples from LC individuals, which suggests oxidative stress situation. Membrane phospholipids (PLs) were increased, probably due to alterations in cell proliferation regulation and invasion mechanisms. Carnitines levels (CARs) were increased in LC patients indicating disturbances in the β -oxidation of fatty acids. This fact is accentuated in patients with a higher smoking exposure, suggesting its influence on the occurrence of these metabolic processes observed in LC. On the other hand, valine and creatine, implicated in succinyl-CoA synthesis and ATP-Creatine system respectively, were the only two altered metabolites in serum of LC patients with an elevated P/Y>75. These metabolites did not show alterations in LC patients with moderate P/Y<35.

Conclusions: The metabolomic analysis of serum samples from lung cancer patients showed a clear differentiation between healthy controls and LC subjects and the influence of smoking exposure. Potential biomarkers of smoke exposure degree influence on LC diagnosis were identified, and their relation with LC pathological mechanisms has been established.

Key Words: metabolomics, lung cancer, smoking exposure

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P24 - Separation and quantification of aliphatic amines in atmospheric particulate matter by ion chromatography (IC)

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Abstract

Purpose: Among the atmospherically-relevant organic compounds, amines have recently received considerable attention because of their acid-neutralizing capacity and their tendency to form toxic compounds. These substances are characterized by a low vapour pressure and reacting with acids lead, like ammonia, to the formation of salts in the particulate phase. It is known that amines have mainly anthropogenic sources, such as animal husbandry, agricultural activity, biomass burning, industry, tobacco smokes. More than one hundred of different substances belonging to this class are emitted from different kinds of sources have been identified in the atmosphere up to now. Methyl and ethyl amines, including mono-, di- and tri- form, are the most common in the atmosphere and have the highest concentrations near major sources. The main objective of this study is the separation and quantification of aliphatic amines in PM₁₀ samples collected during the entire 2013 in the urban background site of the Air Quality Network (AQN) of Lombardy, Milano-Pascal. The analysis of these species has been performed by IC (Ion Chromatography).

Experimental description: Two methods based on IC (Dionex ICS-1000) were developed for the detection of methyl and ethyl alkyl amines (methylamine - MA, ethylamine- EA, dimethylamine - DMA, diethylamine - DEA and trimethylamine - TMA). After the set-up of the methodology, chromatography separation was achieved using a methanesulfonic acid gradient elution on a Dionex CS17 column that has allowed the quantification of the main cations as well.

Results: DMA and TMA were the two species detected with DMA present in slightly higher concentrations. A very fair correlation has been put in evidence between DMA and potassium in the early spring. K is considered, together with levoglucosan, as a tracer for the quantification of wood burning (WB) to PM emissions. It is worth to note that DMA shows higher values in the early spring and during summertime, two periods during which agricultural activities are generally carried out. In fact DMA has a fungicide power and is often employed in the formulation of herbicide used for the shedding on farmlands. DMA at Milano-Pascal is present with a concentration of 0.1-11 ng/m³. During the first episode in spring 2013 the good correlation with K could also be due to some contribution of WB as source of DMA while during summer 2013 agricultural activity is the main source. It is worth to note that the data here presented are the first ones for Milan. In order to better investigate aliphatic amines concentrations in the Po Valley, we are currently carrying out the same analyses on samples collected at Corte de Cortesi, a Air Quality Network site in the middle of the Po Valley where agricultural, and zootechnical activities are predominant. In this site, ammonia (NH₃) measurements are running since 2007, showing the highest concentrations when spreading slurry in agricultural sites are permitted: during these episodes, higher concentrations of amines are expected.

Conclusions: Aliphatic amines have been identified separated and quantified in the aerosol particulate matter. This class of substances is characterized by high toxicity so it is of concerns for human health. Furthermore amines are of interest since they are involved in the formation processes of secondary particulate matter.

Key Words: amines, aerosol particulate matter, ion chromatography, IC

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P25 - Are biosurfactant and chelating agent mixtures good additives for electro-kinetic remediation of multi-contaminated sediments?

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Abstract

Purpose: This study focused on evaluating whether the biosurfactant (Rhamnolipid or Saponin) and chelating agent (Citric acid) mixtures are useful or not for electro-kinetic remediation of multi-contaminated sediments, which contain polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and also heavy metals. Another aim of this study was to reveal if a natural biodegradable biosurfactant could favorably replace synthetic surfactants to favor the organic decontamination of sediments.

Experimental description: The experimental electro-kinetic device consisted of a sediment chamber and two electrode compartments (applied voltage gradient: 1 V.cm^{-1}) filled respectively with two pumps for injecting the aqueous solutions of bio-surfactant and chelating agent mixtures. A reconstituted sediment was prepared by mixing different constituents (73% silt, 5% sand, 19.5% kaolinite, 2.5% organic matter) with an initial pH=8.5, mimicking the properties of a French dredged harbor sediment. Five PAHs (phenanthrene, fluoranthene, pyrene, chrysene and benzo(a)pyrene) and five PCBs (PCB 28, 52, 101, 138 and 180) were added to the dry sediment, which was aged for 4 months. A solution of 5 heavy metals (Cd, Cr, Cu, Pb and Zn) was mixed with the dry reconstituted sediment two days before the electro-kinetic remediation process started. Three tests were performed during 12 days, with a periodic voltage (5 days on, two days off): one run (1) using a mixture of rhamnolipid/citric acid as catholytes and anolytes, one run (2) without rhamnolipid in the cathode compartment and one run (3) using a mixture of saponin/citric acid in the two electrode compartments.

Results: This study showed that the non-ionic biosurfactant (saponin) and the anionic biosurfactant (rhamnolipid) gave almost the same capacity in remediating PAHs (approximately 25% decrease), which did not correspond to our previous researches. Indeed, non-ionic synthetic surfactants (such as Tweens) showed better results for PAH remediation, because they did not counteract the electro-osmotic flow (EOF) (from the anode to the cathode), which is not the case of anionic ones, that electro-migrate towards the anode. After each electro-kinetic treatment, the PAHs had a tendency of moving from the middle to the anode side when the Rhamnolipid and Saponin were used as additives, and so did the PCBs. But the remediation of PCBs was not significant, probably because of the too low concentration of bio-surfactants (1 g.L^{-1}). For heavy metals, the relatively best remediation was revealed when the Rhamnolipid was pumped only into the anode compartment (run n°2), compared to pumping the Rhamnolipid into both electrode compartments (run n°1). It means the ionic biosurfactant may not favor the remediation of heavy metals, probably because of its

adverse effect on EOF. The remediation results using Saponin mixed to citric acid (run n°3) was a little better than that with Rhamnolipid for Cd, Cr and Pb, but for Cu and Zn these two tests were similar. At last but not least, the benefit of the periodic voltage was not visible for this study (particularly on the current intensity), probably because the number of on/off cycles was too few.

Conclusions: These tests show that at the low concentration of Rhamnolipid/Saponin and Citric acid mixtures, the migration and elimination of multi-contaminants after the electro-kinetic remediation process was not significant, which need a higher concentration of bio-surfactants and chelating agent mixtures and also a longer treatment time.

Key Words: Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, heavy metals, bio-surfactant, chelating agent, electro-kinetic remediation

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