ELECTROACROSS Conference
11-12 September 2014 | FCT-UNL, Portugal

WP1 Electroacross final conference
WP2 EK in conservation of cultural heritage
WP3 EK remediation
WP4 Coupling EK to nanoremediation and phytoremediation
WP5 EK nutrient recovery

Advanced Analytical Monitorization Characterization
Book of Abstracts & some outputs of the ELECTROACROSS project

FFCT-UNL, Portugal

11 -12 September 2014
Book of Abstracts & some outputs of the ELECTROACROSS project

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PREFACE

The ELECTROACROSS Conference is to be held in Campus de Caparica, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal, September 11 - 12, 2014. This event corresponds to Work Package 5 of the ELECTROACROSS project, entitled *Electrokinetics across disciplines and continents: an integrated approach to finding new strategies for sustainable development* (FP7-PEOPLE-2010-IRSES/MC-IRSES-269289), which is running from March 2011 to February 2015 and has the following Coordinator and Partners:

Partners: (2) Faculty of Sciences and Technology, University of Algarve, Portugal;
(3) Dep. of Chemical Engineering, University of Málaga, Spain;
(4) Dep. of Civil Engineering, Technical University of Denmark, Denmark;
(5) Dep. of Chemical and Environmental Engineering, Technical University Federico Santa Maria, Chile;
(6) StateKey Lab of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, China;
(7) Centre for Green Chemistry, Monash University, Australia;
(8) Dep. of Management of Ecological-economic Systems, People’s Friendship University of Russia, Russia;
(9) Dep. of Chemistry, IChem & Dep. of Clinical and Toxicology Analysis, Faculty of Pharmacy, Federal University of Minas Gerais, Brazil;
(10) Dep. of Civil and Environmental Engineering, Lehigh University, USA.

This book comprises the Programme, the Abstracts of the presentations for the oral and poster sessions, as well as some of the Abstracts of SCI papers achieved so far.

Acknowledges are due to all those who gave their time and financial contributions to the effort of making ELECTROACROSS a success.

The Organizing Committee
# PROGRAMME

## Part I  ELECTROACROSS - Electrokinetics across disciplines and continents

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Friday, September 12

14:30 – 15:30  In the stars, in the genes, and in the schools: Unsustainable thought / sustainable ideas in the dialogue with nature

Christopher D. Auretta (Dep. of Applied Social Sciences, FCT-UNL)

15:30 – 16:15  Round Table: Alexandra Ribeiro (CENSE-DCEA, FCT-UNL) as moderator

Christopher D. Auretta (Dep. of Applied Social Sciences, FCT-UNL); João Joanaz de Melo (CENSE-DCEA, FCT-UNL); João Simões (Teacher at Colégio Campo de Flores, Collaborator in the Seminar Topics in Contemporary Thought, FCT-UNL); Filipe F. Caetano (Grupo Esporão)

16:15 – 16:30  Closing | Wine tasting

Oral Presentations

Thursday, September 11

09:20 – 10:00  Session 1: Electrokinetic nutrient recovery

Chair: Margarida Ribau Teixeira

O11  Electrochemical process for phosphorus recovery from water treatment plants

Couto N\textsuperscript{1}, Guedes P\textsuperscript{1}, Teixeira MR\textsuperscript{2}, Santos C\textsuperscript{2}, Mateus EP\textsuperscript{1}, Ribeiro AB\textsuperscript{1} (\textsuperscript{1}CENSE, DCEA, FCT-UNL, Lisboa, Portugal; \textsuperscript{2}CENSE – Faculdade de Ciências e Tecnologia, Universidade do Algarve, Faro, Portugal)

O12  Phosphorus recovery from sewage sludge and its ashes: suitability of the electrokinetic process

Guedes P, Couto N, Mateus EP, Ribeiro AB (CENSE, DCEA, FCT-UNL, Lisboa, Portugal)
10:00 – 11:50  
**Session 2: Electrokinetic remediation of organics and inorganics**  
*Chair: José M. Rodriguez-Maroto*

**O21**  
**Electroremediation of soil polluted with drugs common used: use of natural adsorbents in the adsorption-electroremediation technique**  
Hernández-Luis F\(^1\), Vázquez MV\(^2\), Carvajal EG\(^2\), Dévora S\(^3\), Abdalá S\(^3\), Rodríguez-Raposo R\(^1\), Martín-Herrera D\(^3\), Arbelo CD\(^4\)  
(\(^1\)Chem. Dep, Facultad de Ciencias, Universidad de La Laguna, Tenerife, Spain; \(^2\) GIEM, Instituto de Química, Universidad de Antioquia, Medellín, Colombia; \(^3\)Unidad de Farmacología y Farmacognosia, Facultad de Ciencias de la Salud, Universidad de La Laguna, Tenerife, Spain; \(^4\) Dep. Biología Animal, Edafología y Geología, Facultad de Ciencias, Universidad de La Laguna, Tenerife, Spain)

**O22**  
**EKR of copper mine tailings. Evaluating different alternatives**  
Rojo A, Gutierrez C, Hansen HK  
(Dep. Ing. Química y Ambiental, Universidad Técnica Federico Santa María, Valparaíso, Chile)

**O23**  
**The power of power - Electrokinetic control of PAH interactions with exfoliated graphite**  
Qin J, Moustafa A, Harms H, El-Din MG, Wick L  
(UFZ - Helmholtz Centre for Environmental Research, Germany)

**O24**  
**Life cycle assessment of soil and groundwater remediation: groundwater impacts of electrokinetic remediation**  
Nunes LM\(^1\), Gomes HI\(^2\), Ribau Teixeira M\(^1\), Dias-Ferreira C\(^3\), Ribeiro AB\(^2\)  
(\(^1\)CENSE – Faculdade de Ciências e Tecnologia, Universidade do Algarve, Faro, Portugal; \(^2\)CENSE, DCEA, FCT-UNL, Lisboa, Portugal; \(^3\)CERNAS, Instituto Politécnico de Coimbra, Portugal)
Session 3: Coupling electrokinetics with other technologies

Chair: Célia Dias-Ferreira

O31 Phytoremediation response of three miscanthus genotypes
Boléo S, Fernando AL, Barbosa B, Costa J, Duarte MP, Mendes B (UBIA, Dep. de Ciências e Tecnologia da Biomassa, FCT-UNL, Lisboa, Portugal)

O32 Remediation of soil polluted with acetaminophen. Combined adsorption-electrokinetics process
Vargas YR, Carvaja EG, González AS, Naranjo LB, Vázquez MV, Hernandez-Luis F (1GIEM, Instituto de Química, Universidad de Antioquia, Medellín, Colombia; 2Chem. Dep (U.D. Quím.Fís.) Facultad de Ciencias Universidad de La Laguna, Tenerife, Spain)

O33 Electroremediation of PCB contaminated soils with zero iron nanoparticles
Gomes HI, Fan G, Ottosen LM, Dias-Ferreira C, Ribeiro AB (1CENSE, DCEA, FCT-UNL, Lisboa, Portugal; 2Key Laboratory of Soil Environment and Pollution Remediation, ISSCAS, Nanjing, China; 3Dep. of Civil Engineering, Technical University of Denmark, Lyngby, Denmark; 4CERNAS, Instituto Politécnico de Coimbra, Portugal)

14:30 – 15:30

O34 Phytoremediation coupled to electrochemical process for contaminants removal
Couto N, Guedes P, Zhou D-M, Ribeiro AB (1CENSE, DCEA, FCT-UNL, Lisboa, Portugal; 2Key Laboratory of Soil Environment and Pollution Remediation, ISSCAS, Nanjing, China)

O35 Removal of caffeine, oxybenzone and triclosan in aquatic plant-based systems
Ferreira A, Couto N, Guedes P, Mateus EP Ribeiro AB (CENSE, DCEA, FCT-UNL, Lisboa, Portugal)
O36  Methodology for assessment of potential waste dump ground contamination

*Brito MG*, Caetano PS*, Barreiras N* (1Cicege, Dep. Earth Sciences, FCT-UNL, 2CVRM; Geosystems Center, UTL)

15:30 – 15:50  Session 4: Conservation of cultural heritage and use in construction material

*Chair: Nazaré Couto*

O41  Applicability of air pollution control residues in construction materials after electrodialytic pre-treatment

*Magro C*, Kirkelund GM*, Guedes P, Jensen PE, Ottosen LM*, Ribeiro AB* (1CENSE, DCEA, FCT-UNL, Lisboa, Portugal; 2Dep. of Civil Engineering, Technical University of Denmark, Lyngby, Denmark)

Friday, September 12

09:00 – 10:50  Session 5: Modeling of the electrokinetic process

*Chair: Eduardo P. Mateus*

O51  Electrokinetic soil experiments: the circulation current per electroremediation cells as characterization tool of soils

*Hernández-Luis F*, Vázquez MV, Rodríguez-Raposo R, Grandoso D, Pérez M, Ruiz G, Arbelo CD (1Chem. Dep (U.D. Quím.Fís.) Facultad de Ciencias (Sección Química) Universidad de La Laguna, Tenerife, Spain; 2GIEM, Instituto de Química, Universidad de Antioquia, Medellín, Colombia; 3Dep. Biología Animal, Edafología y Geología, Facultad de Ciencias (Sección Biología), Universidad de La Laguna, Tenerife, Spain)
The use of available chemical equilibria software for the prediction of the performance of EKR
Villen-Guzman M1, Gomez-Lahoz C1, Rubio AG1, Garcia JMP2, Alonso CV1, Herruzo FG1, Rodriguez-Maroto JM4 (1Dep. Chemical Eng., University of Málaga, Spain; 2Division of Solid Mechanics, Lund University. Lund, Sweden)

Experimental setup for determination of electroosmotic permeability coefficient of a soil
Gingine V, Cardoso R (ICIST, DECivil, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal)

Modeling of electrodialytic processes of soils containing phosphorus
Paz-Garcia JM1, Ottosen LM2, Ribeiro AB3, Gutierrez-Cordova C4, Hansen HK4, Arce A1, Villen-Guzman M1, Rodriguez-Maroto JM5 (Division of Solid Mechanics, Lund University. Lund, Sweden; 2Dep. of Civil Engineering, Technical University of Denmark, Lyngby, Denmark; 3CENSE, DCEA, FCT-UNL, Portugal; 4Dep. Ing. Química y Ambiental, Universidad Técnica Federico Santa María, Valparaíso, Chile; 5Dep. Chemical Eng., University of Málaga, Spain)

Electrokinetics and zero valent iron nanoparticles: experimental and modeling of the transport in different porous media
Gomes HI1,2,4, Dias-Ferreira C2, Ribeiro AB1, Pamukcu S3, Rodriguez-Maroto JM4 (1CENSE, DCEA, FCT-UNL, Portugal; 2CERNAS, Instituto Politécnico de Coimbra, Portugal; 3Dep. Civil & Environ. Eng, Lehigh University, USA; 4Dep. Chemical Eng., University of Málaga, Spain)
11:10 – 12:10  
**Session 6: Advanced analytical techniques for matrix characterization and contaminants monitoring**

*Chair: Mario Vasquez*

**O61  Multidimensional chromatographic techniques for characterization of environmental samples**

*Mateus EP*, *Ribeiro AB*, *Silva MG*, *Marriott P*  
1CENSE, DCEA, FCT-UNL, Portugal;  
2REQUIMTE- Chemistry Dep., FCT-UNL, Portugal;  
3Centre for Green Chemistry, School of Chemistry, Monash University, Melbourne, Australia

**O62  Analysis of endocrine disruptors compounds in vegetables using SPME and bidimensional gas chromatography**

*Moreira M*, *Silva MG*, *André L*, *Cardeal Z*  
1Chemistry Dep., UFMG, Brazil;  
2REQUIMTE- Chemistry Dep., FCT-UNL, Portugal;  
3Clinical Analysis & Toxicology Dep., UFMG, Brazil

**O63  Detection of low concentration molecules in complex solutions**

*Raposo M*, *Abegão L*, *Ribeiro JH*, *Pimentel R*, *Ribeiro PA*  
CEFITEC, Physical Dep., FCT-UNL, Portugal

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**Poster Presentations**

**P11  Voltammetry of thallium in various electrolytes**

*Ussipbekova EZ*, *Berezovskiy A*, *Seilkhanova GA*  
(Al-Farabi Kazakh National University)
P21 The influence of cathode material on electrochemical removal of trichloroethylene from aqueous solution

Rajic L, Fallahpour N, Nazari R, Alshawabkeh A (Civil & Environ. Eng. Dep., Northeastern University, Boston, MA, USA)

P22 The influence of humic substances on electrochemical degradation of trichloroethylene by Fe/Pd foam cathode

Rajic L, Fallahpour N, Nazari R, Alshawabkeh A (Civil & Environ. Eng. Dep., Northeastern University, Boston, MA, USA)

P23 Electrokinetic remediation of the humic urban soils

Nekrasova MA1, Rodríguez-Maroto JM2, Ribeiro AB3 (1Ecological Faculty of the Peoples Friendship University of Russian, Moscow, Russia; 2CENSE, DCEA, FCT-UNL, Portugal, 3Dep. Chemical Eng., University of Málaga, Spain)

P24 Anionic species transport through the soil (electromigration versus electroosmosis): the case of EDTA

Rubio AG1, Villen-Guzman M1, Paz Garcia JM2, Lahoz CG1, Alonso CV1, Herruzo FG1, Rodriguez-Maroto JM1 (1Dep. Chemical Eng., University of Málaga, Spain; 2Division of Solid Mechanics, Lund University, Sweden)

P31 Effect of capacitive deionization on pH of solution

Kudin DV, Golota VI, Rodionov SV, Abubekerov II (National Science Center "Kharkov Institute of Physics and Technology", Akademicheskaya St., Kharkov, Ukraine)
P31  Electrically induced pore pressures and liquid hydrocarbon oil transport in simulated coastal soil deep layer

*Shrestha RA*¹, *Wang F*¹, *Mateus EP*², *Pamukcu S*¹ (¹Dep. Civil & Environ. Eng, Lehigh University, USA, ²CENSE, DCEA, FCT-UNL, Portugal)

P41  Desalination of danish farm masonry built with bricks by electrokinetic technique

*Conde JF*¹, *Matyščák O*², *Ottosen LM*³ (¹University of Vigo, Campus Lagoas, Vigo, Spain; ²Brno University of Technology, Brno, Czech Republic; ³Dep. of Civil Engineering, Technical University of Denmark, Lyngby, Denmark)

P42  Evaluation of microstructural damage caused by the application of electrokinetic techniques in the desalination of different granites

*Feijoo J, Rivas T, Rosario I, Novoa XR* (University of Vigo, Campus Lagoas, Vigo, Spain)
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ELECTROCHEMICAL PROCESS FOR PHOSPHORUS RECOVERY FROM WATER TREATMENT PLANTS

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Nanofiltration (NF) is a technology that guarantees effective removal of contaminants from drinking water. The products of NF are a clean stream (permeate) and a concentrate stream (membrane concentrate). This last, encloses all the compounds removed by the membrane, including contaminants such as cyanobacteria and cyanotoxins, a consequence of eutrophication problems spread around the world, but also phosphorus (P), an element with socio-economical value.

Membrane concentrate was produced using water from Amoreiras Dam reservoir and was characterized by a high P concentration (approx. 1.4 mg P L\(^{-1}\)) and the presence of toxins produced by *Microcystis aeruginosa*, microcystins variant (MC-LR). Membrane concentrate was subject to the electrodialytic process (ED). Applying a low-level direct current the electrokinetic movement of ions is combined with electrodialysis promoting (i) the movement of analytes towards one of the electrode compartments, where they are concentrated and may be removed and/or (ii) their degradation either in central or in lateral compartments. The application of ED resulted in a significant decrease of cyanotoxins in membrane concentrate and, in some cases, a selective migration towards the catholyte compartment. In other way, the selective accumulation of P in the anolyte compartment opens new possibilities for nutrient recovery. The isolation of P from MC-LR is of extreme importance as cyanotoxins may cause severe health problems due to their acute and sublethal toxicity.
Electrodialytic process is a feasible option for P recovery but the efficiency of the process should be evaluated not only regarding the extent of recovery but also from the concentration of cyanotoxins in the final waste (membrane concentrate or catholyte) allowing a safe disposal or even their re-incorporation in environmental systems (e.g. dam reservoirs).

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PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE AND ITS ASHES: SUITABILITY OF THE ELECTROKINETIC PROCESS

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As population keeps growing, it becomes important to guarantee the supply of staple foods, being necessary to assure good level of nutrients in the soil. Phosphorus (P) is a macronutrient indispensable for plants growth and a non-renewable resource with published data on the lifetime of the exploitable high quality reserves of phosphate rock varying to a great extent, between one hundred and several hundreds of years [1]. Nevertheless, the European Union is almost entirely dependent upon imports, with China, Jordan, Morocco, South Africa and USA controlling 85% of global phosphate reserves [2]. This makes the development new strategies for P recovery for further reuse one of the new challenges. Sewage sludge (SS) and sewage sludge ash (SSA) from waste water treatment plants (WWTP) may contain contaminants or unwanted elements regarding specific applications, but they also contain secondary resources of high value. Using these wastes as a P resource, while removing the contaminants, seems a sustainable option.

The electrokinetic (EK) process can be an effective technique for removing contaminants and recover P from SS and SSA. The application of a low-level direct current onto the matrices results in both electroosmotic and electromigration flows, which are able to induce the migration of ions. For this reason, phosphate selectively accumulates in the anolyte allowing its recovery. EK remediation was applied at a laboratory scale, in SS and SSA and the set of major parameters studied.

This communication aims to make an overview of the results achieved so far on the feasibility of EK process to recover P from WWTP target wastes.
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References


ELECTROREMEDIATION OF SOIL POLLUTED WITH DRUGS COMMON USED: USE OF NATURAL ADSORBENTS IN THE ADSORPTION-ELECTROREMEDIACION TECHNICAL.

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Increasingly, soils suffer from contamination by external agents. These include, among others, the drugs in common use such as the non-steroidal anti-inflammatory drugs NSAIDs (paracetamol, ibuprofen, naproxen, ketoprofen, aspirin, diclofenac, etc...). One of the dangers of the presence of these drugs in the soil is its mobility (due to rainwater, or other fluids) that crawl them to aquifers, rivers, lakes, networks of sewerage. This phenomenon is revealed above all in large cities where there is less control of discharges.

Our interdisciplinary research groups are working on the study of this phenomenon and as hindering a form natural and little aggressive with the environment. This has been one of the objectives proposed the international network RIARTAS (Ibero-American network for the use of waste industrial for treatment of soil and water pollution) whit help of the CYTED (IBERO-AMERICAN PROGRAMME FOR SCIENCE, TECHNOLOGY AND DEVELOPMENT).
We present some preliminary studies on the use of natural adsorbents (dried orange and lemon crust, cork, sawdust, bark of banana plantations, etc.). Studies consider the following steps:

1. Choose drugs to study and your way of quantifying them take into account the change in pH that may occur during the Electrokinetic process (the techniques most used by its features have been V-UV spectroscopy and voltammetry in its many variants).

2. Do a study of the adsorption of the system soil - drug building for this purpose corresponding isotherms.

3. Choose the conditions that carry out the process of electro-remediation (solvents, time of contact, applied electrodes to be used, the cell design, composition of the solutions of the electrodic chambers, extraction and subsequent quantification of the drugs, etc.)

4. Combine the two techniques: electro-remediation and adsorption. This is the point at which we find ourselves and that is giving us more problems. However, we are optimistic on getting the appropriate conditions for successful implementation of this method.
EKR OF COPPER MINE TAILINGS. EVALUATING DIFFERENT ALTERNATIVES OF ELECTRIC FIELDS

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Due to the magnitude of the mining activity in Chile, it becomes necessary to find solutions to mitigate the impact of mining waste on the environment. One method that could be suitable for remediation of mining wastes is the use of electric fields for the removal of metals, the so-called electrochemical remediation: electrokinetic or electrodialytic remediation (EKR or EDR). This principle has been used successfully during around 20 years for the treatment of heavy metal polluted soil. Especially metals such as copper, zinc, lead and arsenic have been removed or concentrated when applying electric fields—and these metals are typically also found in mining waste. The use of this remediation technology will imply the periodic application of the method in order to remove the additional soluble copper that will be generated with time. Therefore, the remediation action for this heterogeneous solid waste is to remove the soluble copper in the tailings and in this way making the final residue more stable.

In this work an EKR cell for copper mine tailings using different types of electric fields was analysed. The analysis includes: EKR with a) direct current fields, b) sinusoidal electric field obtained by applying simultaneously continuous-alternating voltages (at both high and low frequencies), c) pulsed electric fields, and d) the use of bipolar electrodes. Furthermore, combinations of the different conditions have also been tested for some remediation cases.

According to the conditions studied in this investigation, the laboratory results showed that a high frequency sinusoidal electric field improves the EKR process, and increasing the effective voltage improves the remediation action, especially when a polarity inversion is present, which reduces polarization during the process.
THE POWER OF POWER:

ELECTROKINETIC CONTROL OF PAH INTERACTIONS WITH EXFOLIATED GRAPHITE

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Polycyclic aromatic hydrocarbons (PAH) are commonly found in oil field produced waters. Without adequate treatment PAH contaminate the ecosystem and cause deleterious effects to ecosystem and human health. Various treatment approaches for process water have been developed including chemical modifications to adsorbents. Among them, exfoliated graphite (EG) has been attracting particular interest. Having a low density, a high surface area and wide pore size distribution of 2 nm to 10 µm, EG exhibits an exceptional sorption capacity for petroleum and its constituents. Due to its comparably high cost, however, novel approaches hybridizing sorption with physical and biological treatment approaches are needed. Here we use EG as a carbonaceous model sorbent in order to assess the effect of weak direct current (DC) electric fields and on the EG sorption capacity for the PAH phenanthrene. When an electric field is applied to a matrix submersed in an ionic solution, it invokes electromigration, electrophoresis, and electroosmosis (EOF). EOF is the surface-induced movement of pore fluids in an electric field, usually from the anode toward the cathode. EOF is more efficient in fine-grained (with meso- and micropores) than in macroporous materials. The conductivity of fine-grained matrices for pressure-driven (e.g. hydraulic) liquid flow is extremely small and leads to quasi stagnant water in micro- and mesopores. Molecular diffusion hence is limiting both access of sorbates to and release of sorbates from such pores as potential sites of high
sorptive capacity for sorbates. Hence, EG-filled micro-reactors were exposed to a weak DC in presence of PHE to challenge the hypothesis that DC-fields may lead to increased EOF-mediated PHE transport to poorly accessible EG sorption sites and to increased sorption rates and/or decreased desorption rates of as compared to DC-free controls. Our data confirm this hypothesis. They show that EOF leads to increased PHE entrapment in EG-pores and both, to tenfold increased sorption rates and > 99% reduced desorption rates in presence of DC. Such ‘power of power’ may allow for tailor-made regulation of the sorption/desorption kinetics of chemicals to/from sorbents e.g. in water treatment or in biotechnology to control the bioavailability of substrates to transforming microorganisms.
LIFE CYCLE ASSESSMENT OF SOIL AND GROUNDWATER REMEDIATION: GROUNDWATER IMPACTS OF ELECTROKINETIC REMEDIATION

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The growing concern about the sustainability of soil remediation technologies and operations lead to the development of different support decision methods. Life cycle assessment (LCA) methodologies have well-developed methods for assessing environmental impacts for emissions to air, surface water, and surface soil, but deep soil emissions and emissions to groundwater have received little attention. Regional impact of groundwater extractions have largely not been considered in LCA as well, nor their relation to surface water bodies and groundwater-dependent ecosystems. These aspects are now compulsory in the management of water resources in Europe, under EU Water Framework Directive. Future developments in LCA will necessarily have to include these relations in the characterization of the impacts. Given the strong retardation that many pollutants undertake in the soil, the temporal factor is relevant in the groundwater compartment, as contamination may extend for decades. Moreover, groundwater contamination due to industrial sources, including soil remediation, tends to be spatially concentrated, dispersing from the point of origin depending on
hydrogeologic conditions, soil retention capacity, pollutant’s degradation rates, and time. Exposure to contaminated groundwater is frequently assessed by modelling, however the proposed models require detailed information about soil properties, which is usually not available, nor is it possible to obtain in the scope of a life-cycle assessment. Simpler methods are therefore needed. The present article discusses some of these alternatives, in particular applied to soil remediation with electrokinetic methods. The use of in situ electrokinetics for the remediation of fine-grained soils requires contaminants to move from their initial location to an electrode. The migration path can be long and there could be stagnant zones between wells where the rate of migration is slow, both of which can result in an incomplete remediation and to potential impacts on groundwaters.
PHYTOREMEDIATION RESPONSE OF THREE MISCANTHUS GENOTYPES TO SOILS CONTAMINATED WITH ZINC, EFFECTS ON THE BIOMASS YIELDS AND QUALITY

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*Miscanthus* is a woody rhizomatous C4 grass originated in South-East Asia and was initially imported to Europe as an ornamental plant. It is a perennial plant, related to sugarcane, with an estimated productive lifetime of at least 10-15 years, and both the stems and leaves of the crop can be harvested annually and used for bioenergy or biomaterials production. It is characterized by relatively high yields, low moisture content at harvest, high water and nitrogen efficiencies and an apparently low susceptibility to pests and diseases. *Miscanthus* has also been described as tolerant to heavy metals contaminated soils and able to take up and accumulate some metals (e.g. Zn) in its biomass. In this perspective, *Miscanthus* can be used as a remediation technology to restore or attenuate and stabilize heavy metal contaminated sites while bringing additional revenue to owners. This phytoremediation technology can also be coupled with other remediation technologies, such as electrokinetic, to trap the mobilized heavy metals, due to its deep and dense root and rhizome system.

In this context, this research work aims to study the phytoremediation response of three *Miscanthus* genotypes (two species - *Miscanthus sinensis* and *Miscanthus floridulus*, and a hybrid – *Miscanthus × giganteus*) to soils contaminated with zinc (450 and 900 mg Zn.kg⁻¹ dry mass). Results showed that growth and biomass productivity of *M. x giganteus* and *M. floridulus*, but not of *M. sinensis*, were negatively affected by the zinc contamination. Among genotypes, *M. x giganteus* was the most productive, followed by *M. floridulus*. *M. sinensis* was the lesser productive genotype. Biomass obtained in Zn contaminated soils presented significantly higher zinc content then biomass from non-
contaminated soils, thus showing phytoextraction, accumulation and translocation capacity to the aerial biomass. The several fractions, stems, leaves and panicles, presented similar Zn contents. However, the increased accumulation of zinc in the aerial biomass can be detrimental for its use and economic valorization. Nevertheless, the prospect of the valorisation of the Miscanthus aerial biomass, for bioenergy or bio-products production purposes, could lessen the financial costs of soil remediation, compared to the traditional physical – chemical processes, with the associated revenue of environmental benefits.
REMEDICATION OF SOIL POLLUTED WITH ACETAMINOPHEN. COMBINED ADSORPTION-ELECTROKINETICS PROCESS

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Emerging contaminants are an issue of growing concern in relation to their presence in the environment, especially in water. An important point to reduce their presence in the environment is related to proper handling of such drugs, to prevent available directly on soil and water sources. In the case of soils it is interesting analyze the adsorption degree of these compounds and the possibility to remove them using an electric field.

The use of modified residues for adsorbing contaminants has been the subject of numerous studies due to the possibility to build economic systems of treatment. These adsorbents can be constructed from sawdust, which has been shown to be effective in removing a variety of contaminants.

In this paper results obtained with a combined system to study the possibility of removing acetaminophen (paracetamol) present in a volcanic soil is presented. Solutions in the range 50 to 400 ppm were used. The adsorbent was prepared from pine sawdust which was processed to have a uniform particle size and subsequently chemically treated with a solution of 5% formaldehyde for the purpose of increasing its adsorbent capacity.

The soil selected for the study was characterized to assess the amount of organic matter, conductivity, pH, cation exchange capacity, etc.
Acetaminophen quantification was performed spectrophotometrically at 242.5 nm and by cyclic voltammetry using a graphite electrode as a working electrode, following the current signal at 0.5V (vs SCE).

For the electrokinetic study, a electric field of 1-2 V/cm was applied for different times (2 to 24 h) monitoring the electrolysis charge and analyzing the concentration of residual acetaminophen in the electrode chambers and in different regions of the contaminated soil as well as on the adsorbent.

Preliminary results indicate that it is possible to consider the combined system for treatment of soil contaminated with this type of emerging contaminants.
ELECTROREMEDIATION OF PCB CONTAMINATED SOILS WITH ZERO VALENT IRON NANOPARTICLES

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Polychlorinated biphenyls (PCB) are persistent organic pollutants (POP) that accumulate in soils and sediments. These contaminated soils and sediments are an important environmental problem, with a global dimension. Currently, there is a need to develop new, sustainable and cost-effective solutions for the remediation of PCB contaminated soils. Zero valent iron nanoparticles (nZVI) were considered promising for the remediation of contaminated soils and groundwaters, targeting a wide range of contaminants, and especially PCB. However, critical issues related to their limited mobility remain unsolved. A direct current can be used to enhancing the nanoparticles transport, based on the same principles of electrokinetic remediation (EK). Integrating both technologies, the role of the direct electric current would be to get nZVI into the soil for in-situ transformation and subsequent destruction of the contaminants, instead of aiming at the contaminants transport for removal.

This work integrates all experimental work made for the electroremediation of PCB contaminated soil, coupling electrokinetics with nZVI, starting from the tests with bimetallic Fe/Pd stabilized nanoparticles and including the comparison between the traditional three-compartment
electrokinetic setup and the new two-compartment electrodialytic (ED) setup developed at the Technical University of Denmark (DTU).

The experiments with EK and Fe/Pd nanoparticles were not encouraging for scale up of the process, with only 20% PCB removal. The electrodialytic setup showed best removals (>75% in real contaminated soils) and showed several advantages, such as a higher PCB dechlorination in contaminated soil, in a shorter time, with lower nZVI consumption, and with the use of half of the voltage gradient when compared with the traditional EK setup. The suspended electrodialytic remediation combined with zero valent iron nanoparticles (nZVI) could be a competitive alternative to the commonly adapted solutions of incineration or landfilling. The ED setup allowed a uniform distribution of the nano iron in soil, while there was iron accumulation in the injection reservoir in the EK setup.
PHYTOREMEDIATION COUPLED TO ELECTROCHEMICAL PROCESS FOR CONTAMINANTS REMOVAL

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Soil metal contamination arising from mining operations can be considered as a major threat to land use. Phytoextraction is a viable option to rehabilitate these contaminated soils but the bioavailability of contaminants can represent a limitation that might be overcome by the electrokinetic process (EK).

Phytoremediation, using Indian mustard and ryegrass, was coupled with EK and/or phosphate amendment aiming to remediate a Chinese mine soil contaminated with arsenic (66 mg As kg⁻¹) and antimony (546 mg Sb kg⁻¹). At the end of 15 days, soil pH slightly changed in cathode and anode compartments and no negative effect was found in biomass production. Ryegrass accumulated 85 ppm of As and 116 ppm of Sb whereas Indian mustard accumulated 109 ppm of As and 170 ppm of Sb. Phosphorus amendment enhanced metalloids uptake with higher effectiveness for Indian mustard (approx. more 80 ppm of each metalloid). EK together with P-amendment provided a slight increase in total metal uptake with ryegrass accumulating 106 and 144 ppm and Indian mustard 211 and 276 ppm of As and Sb, respectively. EK slightly decrease the concentration of available nutrients in soil comparing to the treatment with only plant. In terms of enzymatic activity, differences were found for Indian mustard with a decrease for neutral phosphatase and an increase for urease, in all applied treatments, except plant alone.

Phytoremediation coupled with EK and/or phosphate amendment can be an effective option to reduce contamination levels in mining areas but its efficiency depends on time constraints. This work
aims to enlarge the discussion about potential, limitations and future perspectives of application of hybrid technologies.

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REMOVAL OF CAFFEINE, OXYBENZONE AND TRICLOSAN IN AQUATIC PLANT-BASED SYSTEMS

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The use of pharmaceuticals and personal care products (PPCPs) is growing as they are used not only for treatment but also for prevention of illnesses. In wastewater treatment plants (WWTPs) many PPCPs are not completely degraded/removed, which contributes for their frequent detection in e.g. salt marsh areas. These areas may be considered a sink, source and cycling center of contaminants on the receiving water body flow rate. The aim of the present work was to study, at the microcosm level, the potential of salt marsh plants Spartina maritima and/or Halimione portulacoides for the removal of caffeine (CAFF), 2-hydroxy-4-methoxybenzophenone (MBPH) and triclosan (TCS). Experiments had two main aims (i) the optimization of biological treatment technologies in WWTPs by simulating constructed wetland composed by plants and light expanded clay aggregates (LECA) and (ii) the simulation of natural estuarine environment and study of dispersion mechanisms and “natural” remediation potential of target PPCPs.

Either in WWTP or in estuaries the presence of a physical support can help to decrease contaminant levels mainly through sorption processes. The tested salt marsh species also showed potential to directly or indirectly promote the remediation of contaminants. In any case the remediation potential and dispersion mechanism are highly dependent from the characteristics of contaminants like octanol-water partition coefficient (Log $K_{ow}$) and solubility. For example, when arriving to the estuary CAFF will mainly appear in the liquid phase whereas MBPH and TCS in the sediments (solid phase).
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METHODOLOGY FOR ASSESSMENT OF POTENTIAL WASTE DUMP GROUND CONTAMINATION

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In Portugal sealed waste dumps are still an environmental hazard to groundwater and ecosystem since most of these deposits are located in high vulnerability aquifer areas and protected ecosystem areas, as water stream valleys or inside old open pit quarries, without any foundation protection. Although some of these infra-structures are already integrated in municipal landfill waste management systems and, consequently, controlled by landfill monitoring plans, undesired environmental problems related to soil and water contamination often arise due to lack of information about dump foundation and local geological and hydrogeological characteristics and properties.

This paper presents a two-step methodology designed to: (i) identify the state of waste dump facilities in order to suppress the lack of information concerning potential leachate origins and; (ii) proceed with geological and groundwater modeling in order to assess potential contamination plumes and support any necessary remediation and clean-up strategies.

In the first step, an electrical geophysical survey is performed to assess internal saturation state of the infrastructure and depth of foundation dump. Results gathered from geoelectrical survey confirmed that the waste dump was fully saturated and consequently, leachate production is highly probable and ground contamination expectable.

In the second step, the geological structure is characterized and groundwater modeling is performed in order to simulate time-series contamination plumes and paths. The quality of the obtained results is highly dependent on the quality of this geological and hydrogeological characterization since
potential contamination of soils and groundwater is mainly controlled by geological structure and physical characteristics of media (such as lithology, porosity and permeability) and by local fluid dynamics (such as groundwater level, flow direction and hydro-geochemistry).

The methodology was applied to an old waste dump integrated in a municipal waste management system and located in an urban area of Oeiras, near Lisbon. The results obtained from this two-step evaluation has provided crucial information for future developments, mainly for human health and ecosystems risk assessment and for containment and/or cleanup strategies including selection of the best procedures and available remediation technologies.
APPLICABILITY OF AIR POLLUTION CONTROL RESIDUES IN CONSTRUCTION MATERIALS AFTER ELECTRODIALYTIC PRE-TREATMENT

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Air Pollution Control (APC) residues are one of the waste products from flue gas cleaning in Municipal Solid Waste Incineration (MSWI). There are different APC residues, depending on the design of the plant (wet or semi-dry systems). They are considered hazardous due to their contaminants content, namely leachable heavy metals, salts and/or dioxins. Because of their hazardousness and instability, APC residues constitute an environmental problem and, consequently, stabilization prior disposal is required. APC residues can be further reused, if the contaminants are successfully removed or stabilized, they may be a valuable resource, for instance, in the production of concrete. The electrodiatylic (ED) process can be used as a pre-treatment, before the incorporation of APC residues in construction materials. A set of eight ED experiments were conducted with two different ashes for 7 days. The APC residue (100 g) mixed with deionized water (350 mL) and a set of major parameters were tested: current density (0.1 or 1.0 mA cm\textsuperscript{-2}) and number of cell compartments (2 or 3). Obtained results showed that after 7 days of ED process the ash pH stayed alkaline, so, the remediation was difficult but the immobilization of the heavy metals was promoted. The two types of APC residues were submitted a stabilization/solidification (S/S) technique, where, 5% of Ordinary Portland Cement was replaced by residues of APC in mortars, with or without ED pre-treatment. Porosity, density, compressive strength, heavy metals leaching and chloride were tested. By analysing the studied parameters, it is possible to say that for the wet gas cleaning systems the best
option prior its reuse is to apply a pre-treatment, since the heavy metals leaching decreased. In the other hand, for semi-dry systems the, e.g., compressive strength decreased after a pre-treatment, therefore, for this type of APC it is thus preferable to aggregate the raw residue. This study suggests new possibilities for this APC waste reuse, presenting great advantages in the waste management system.

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ELECTROKINETIC SOIL EXPERIMENTS: THE CIRCULATION CURRENT PER ELECTROREMEDIATION CELLS AS CHARACTERIZATION TOOL OF SOILS

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This communication contains preliminary results that are part of a series of investigations to get correlations between parameters determined in simple Electrokinetic experiments with soils of volcanic origin of Tenerife (Canary Island, España) and of Medellin (Antioquia Department, Colombia) and their edaphic characteristics.

The application of an electric field between two inert electrodes include a sample of damp soil, produces a series of Electrokinetic phenomena that promote the transport of particles, both charged as not loaded. It seems logical to think that this electrical disturbance could be used as an useful tool for the characterization of soils (electro - characterization).

To carry out these studies one should analyze the variation in time of the different experimental parameters obtained during a typical electrokinetic, such as electrical resistance experiment the moist soil in the cell, the circulated current intensity (if work constant applied to potential) or the variation of potential (if we work with a constant current), etc. In some cases it is a comprehensive analysis of both electrical and physicochemical quantities simultaneously.
In the present work, the current electrokinetic obtained for several soils of the island of Tenerife and of the Medellin city were mathematically adjusted to a model similar to the one that represents the charging of a capacitor in an RC circuit. The constants obtained in this setting, tried to correlate with different physico-chemical properties of the soils studied. The objective of this work is to use these correlations to predict an approximate the characteristics of other soils without resorting to elaborate common procedures in soil laboratories.

Obviously, once many more soils are studied and many more parameters are analyzed, one can have a broader characterization of soils. In this sense, we intend in the not-too-distant future implement a study of neural networks to predict yet measured parameters.
The use of available chemical equilibria software for the prediction of the performance of EKR

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Risk assessment aims for the prediction of the mobility of contaminants, and these are usually based in lab essays together with mathematical modelling. Also the feasibility studies of most techniques, require similar tools. Frequently the lab characterization is based in the chemical fractionation of the contaminants based on their mobility under different chemical reagents. Probably the most frequent fractionation technique for heavy metal contaminated soils is the BCR [1].

The use of chemical equilibria software helps to understand the processes involved in the contaminant transport during electrokinetic remediation. Most mathematical models used for the simulation of electrokinetic decontamination assume local equilibrium between the chemicals present in the aqueous phase. In other cases also equilibrium is supposed between the chemical species present in the aqueous phase and the solid matrix.

In this work, we compare the results of batch extraction experiments with those obtained using Visual MINTEQ [2]. This is a free software that allows a reliable simulation of the chemical processes involved in the water-soil systems such as solubility, sorption, etc.

We found that even when the main contaminant behaviour is in accordance with the local equilibrium assumption, the mobilization of other metals, such as Ca and Mg, that are also present in important concentrations, are affected by kinetic limitations. These kinetic limitations have important effects in the overall behaviour of the system. Thus, if ignored, important flaws will appear
in the predictions of the model with respect to those toxic species that could be considered to behave under local equilibrium.


   http://www2.lwr.kth.se/English/OurSoftware/vminteq/index.html
EXPERIMENTAL SETUP FOR DETERMINATION OF ELECTROOSMOTIC PERMEABILITY COEFFICIENT OF A SOIL

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Electrokinetic treatment can be a very beneficial technique to dewater or decontaminate the fine grained soils of very low hydraulic permeability. When the electric potential is introduced in the soil through the electrodes, there is a movement of the charged species present in the diffuse double layer to the oppositely charged electrodes. This ionic drift will drag the surrounding liquid with it. For unidirectional flow along the position $x$, water flow $q$ can be described by Equation 1, where $k_e$ is electroosmotic permeability coefficient, measured when water percolates the soil under constant voltage gradient $dV/dx$.

$$q = k_e \frac{\partial V}{\partial x}$$  \hspace{1cm} (1)

During the electrokinetic treatment, Hydrodynamical consolidation occurs if soil is saturated and it experiences volume changes since there is a change in effective stress due to changes in interstitial pressure. In this case unidirectional water flow $q$ can be described by Equation 2, where $u$ is the increment of interstitial pressure, $k_e$ is already explained and $k_h$ is the hydraulic conductivity measured when water percolates only due to differences in water potential.

$$q = \frac{k_h}{k_e} \frac{\partial u}{\partial x} + k_e \frac{\partial V}{\partial x}$$  \hspace{1cm} (2)

Electroosmotic permeability is therefore one soil property which should be known for efficient planning of this treatment and predicting its consequences in the field. In this paper, a brief review of various laboratory determination methods of $k_e$ from the past has been given. This paper also describes the apparatus and procedure of a simple technique proposed for the determination of $k_e$. 

where a constant DC voltage gradient is applied in a modified oedometer cell and both vertical displacement and volume of fluid collected at the bottom of the sample are used in the calculation. Commercially available Kaolin soil was tested for different void ratios and initial water contents to simulate the site conditions. The values obtained were found similar to those in the literature. Thus it was observed that using this apparatus the test is relatively fast and simple to perform in the laboratory.
MODELING OF ELECTRODIALYTIC PROCESSES OF SOILS CONTAINING PHOSPHORUS

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Phosphorous is an essential constituent in natural soil. Electrokinetic remediation treatments may produce the migration of phosphorous-containing compounds (PCCs), as well as changes in the chemical composition of the minerals containing this element. The presence of PCCs in the soil may play an important role in the efficiency of electrokinetic remediation techniques, affecting, for example, to the buffering capacity of the soil and to the optimal pH for the remediation. In addition, due to the increasing demand of phosphorus as a fertilizer agent, the electrochemically induced solubilization and migration of phosphorous during electrokinetic treatments may be considered as a technique for the recovery of this element to be reused for agricultural purposes.

The transport of PCCs strongly depends on their chemical speciation. Phosphorous forms very insoluble minerals with almost all cations, except for alkaline ions, protons and ammonium ions. The chemical affinity with calcium ions to form insoluble apatite minerals is remarkable. Enhanced techniques, such as acid-enhanced and/or electrodialytic techniques, are needed in order to increase the mobility of phosphorous compounds in the soil. In this work, a simulation-based study of the chemical speciation of phosphates and other phosphorous species during electrodialytic soil
remediation processes is presented. The system modeled here includes a comprehensive set of feasible chemical reactions involving phosphorous in different oxidation states. Both homogeneous aqueous complexation and heterogeneous precipitation/dissolution reactions are included. Simulation results for the efficiency of the electrodialytic treatment are presented for different scenarios, i.e. soils with different PCCs speciation.
ELECTROKINETICS AND ZERO VALENT IRON NANOPARTICLES: EXPERIMENTAL AND MODELING OF THE TRANSPORT IN DIFFERENT POROUS MEDIA

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Since the late nineties, with the development of nanotechnologies, zero valent iron nanoparticles (nZVI) were considered a promising step forward in soil and groundwater remediation, due to their size and reactivity that allowed the possibility of their injection in contaminated areas. However, nZVI have an important drawback – their limited mobility in porous media. Direct current can be used to enhance nZVI transport, based on the same principles of electrokinetic remediation (EK). Previous works on the nZVI assisted transport and modeling in sands focused only on electrophoresis as the predominant transport mechanism.

In this work are presented the experimental results of nZVI assisted transport on mixtures of kaolin and glass beads to represent different porous media, as well as a generalized physicochemical and numerical model.

In the experiments, a low level direct current was used to enhance poly(acrylic acid) sodium salt coated nZVI in a modified electrophoretic cell (Econo-Submarine Gel Unit, model SGE-020). The cell was equipped with internal auxiliary electrodes (0.25 mm diameter platinum wire electrodes...
embedded in the base plate of the sample tray) and a silver chloride (Ag/AgCl) reference electrode. The results showed that there were higher concentrations of iron across the test bed when direct current was applied. In all the experiments with glass beads there is a very well defined peak of concentration near the injection point. This is potentially due to the aggregation or fast corrosion of the iron nanoparticles, or to both phenomena.

The model consists in the Nernst–Planck coupled system of equations, which accounts for the mass balance equation of ionic species in a fluid medium, when diffusion and electromigration are considered in the ions transport process. In the case of the stabilized nZVI (with negative charge), diffusion and electrophoretic terms have been considered. In both cases, also the electroosmotic flow was included in the equation. The model allowed detecting that, in some cases, an important fraction of the nZVI tends to aggregate, when the concentration is high relative to the available pore volume, becoming immobile. However, this aggregated mass clearly decreases in the presence of a direct current.
MULTIDIMENSIONAL CHROMATOGRAPHIC TECHNIQUES FOR CHARACTERIZATION OF ENVIRONMENTAL SAMPLES

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There is a growing resurgence of multidimensional gas chromatography (MDGC). This is either due to the emergence of comprehensive two dimensional gas chromatography (GCxGC) in the last decade, as a solid technique and to the recent introduction, by many GC instrument companies, of new devices capable of delivering MDGC with high accuracy (e.g. new Deans switch devices and modulators), supported by hardware and software development. This resurgence has been driven by the search of improved separation performance for analytes in complex samples. MDGC allows separation of complex mixtures by using multiple columns with orthogonally different stationary phases, enabling the separation of complex mixtures that cannot be separated using a single column. The heart-cut method (peak cutting and the selective transfer of peaks or chromatogram sections onto a second column) and the continuous two-dimensional chromatography (comprehensive chromatography) are the common used techniques in MDGC. Multidimensional GC may also be extended to become a preparative technique based on capillary columns, allowing separation and enrichment of components from complex samples for identification purposes. The characterization biogenic emissions from rice and environmental samples (atmospheric particles and soils), among others will be used to demonstrate the applicability of MDGC operational modes that can be
achieved with the longitudinal modulation method. The increased resolution and sensitivity achieved is an advantage, which would be beneficial for complex samples and trace analysis.

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ANALYSIS OF ENDOCRINE DISRUPTORS COMPOUNDS IN VEGETABLES USING SPME AND BIDIMENSIONAL GAS CHROMATOGRAPHY

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Some organic micro-contaminants are often found in foods which can cause dysfunction in the endocrine system of humans and animals and are therefore classified as endocrine disruptors compounds (EDC). Phthlates and alkylphenols are classified as EDC. Food contamination by phthalate can occur due to migration of these compounds present in packaging for food. Alkylphenols are commonly present in pesticides and the contamination can occur due to the use of such compounds in the cultivation of vegetables. The EDC are present in low concentrations in foods and the development of highly sensitive analytical techniques is required for its quantification. This study describes the development of a new method for analysis of EDC, phthalates and alkylphenols in frozen foods wrapped in plastic packages. The analyses were performed by solid phase microextraction (SPME) using comprehensive two-dimensional gas chromatography with flame ionization detector. To determine the EDC 10.0 g of sample was transferred to a beaker containing 40 mL of water, which was stirred at room temperature for 30 min. An aliquot of 15 mL was transferred to SPME vial in which the extraction was made by direct immersion of a polyacrylate fiber. For this, extraction temperature of 65 °C and extraction time of 30 min were used. The validation was performed following EURACHEM recommendations. The developed method shows high separation efficiency and peak resolution. The limits of detection for the studied compounds
ranged from 0.07 to 0.3 μg L$^{-1}$. The precision was evaluated in intra- and inter-day assays at concentrations of 1.0 and 5.0 μg L$^{-1}$. The analytical curves showed that the residues were homoscedastic and independent with normal distribution for all compounds.
DETECTION OF LOW CONCENTRATION MOLECULES IN COMPLEX SOLUTIONS

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Water pollution is one of the biggest contemporary problems of mankind and it is a major cause for death and disease. Conventional pollutants are pesticides, industrial intermediates and pharmaceuticals and personal care products (PPCPs). Nevertheless, no commercial sensors for monitoring and detecting these pollutants have been developed so far due to the difficulty to detect very low concentrations in complex solutions. To study the detection of a molecule at low concentrations, a sensor that detects deltamethrin in a solution with a concentration of the order of micro and nano molar was developed, by measuring the electrical impedance, with a fixed frequency of 100 Hz, which presents a linear behavior by concentration per decade. This sensor has a sensitivity of $41.1 \pm 0.7 \, \text{k}\Omega$ per decade of concentration for an immersion time greater than 2 minutes and with a reproducibility error around 2%. To detect in a complex solution a low concentration of a pharmaceutical product, ibuprofen, an array of sensors were prepared and the electrical properties characterized. The obtained results and conclusions will be shown in this presentation.
VOLTAMMETRY OF THALLIUM IN VARIOUS ELECTROLYTES

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Thallium is used as a catalyst in making alloys, optical lenses, jewelry, low temperature thermometers, dyes and pigments and in scintillation counters. Its compounds have also been used as medicines, rodenticides and insecticides. It is extremely toxic to humans, plants and animals and plays no role in their metabolisms. Soluble multivalent thallium compounds, e.g. thallium(I) sulfate, nitrate, acetate and carbonate are very toxic because they are easily absorbed into the human body by skin contact or ingestion. It should be noted that high purity thallium is also used as a source of β-radiation in radioisotopic devices. In this regard, investigations in the field of electrochemical methods for obtaining high-purity thallium are of particular relevance.

This paper presents the results of the study of the electrochemical behavior of thallium in sulphate, nitrate and acetate solutions. The measurements were made using AUTOLAB-30 potentiostat-galvanostat with computer control station. Glassy carbon electrode was used as working electrode (GC, the electrode area of 1 cm²), silver chloride electrode was used as the auxiliary electrode (comparison), the anode - platinum plate. Cyclic polarization curves were obtained at various scan rates at different speeds of stirring in the temperature range of 25-65 °C, deposition of thallium was carried out in potentiostatic and galvanostatic mode (thallium salt concentration was 0.001 mol L⁻¹).

Optimal mode of discharge-ionization processes of thallium from sulfate, nitrate and acetate solutions flowing in the diffusion area. Maximum conventional current output is specific for thallium sulfate. Increasing the concentration of thallium electrolyte leads to an increase in current efficiency, and increase in temperature accelerates the electrochemical reaction. Based on the results, sulfate electrolyte with background electrolyte (Na2SO4) on glassy carbon was chosen for further
researches. It was found that the anode is passivated by dark brown film of thallium (III) oxide during electrodeposition of thallium in alkaline and neutral media, at pH 1-2 passivation does not occur. The results of electrochemical studies can be used in optimization of the technology of refining rough thallium.
THE INFLUENCE OF CATHODE MATERIAL ON ELECTROCHEMICAL REMOVAL OF TRICHLOROETHYLENE FROM AQUEOUS SOLUTION

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Electrochemical technologies for groundwater treatment use a low-level direct current (DC) through electrodes in a well which enables manipulation of groundwater chemistry through electrolysis to create conditions favorable for either reduction or oxidation of the contaminants. There are several advantages to this approach: 1) it is sustainable and driven by a renewable energy source (if solar power is used to generate DC), 2) it does not require the addition of solutions or chemicals into groundwater, making them environmentally friendly, and 3) the rates of redox reactions can be controlled by adjusting electric current intensity. Development of an electrochemical reactor within the aquifer for the sustained electrolysis is the first step in development of electrochemical technologies. Here we present the influence of cathode material on trichloroethylene (TCE) transformation in aqueous solution by an electrochemical flow-through reactor. The efficiencies of TCE degradation by Fe, Cu, and Ni foam cathode were 43.5%, 56.2%, and 68.4%, respectively. The normalized pseudo-first-order rate coefficients, $k_{sv}$ (L m$^{-2}$ min$^{-1}$) were 1.13x10$^{-4}$, 1.16x10$^{-4}$, and 1.58x10$^{-4}$ for Fe, Cu and Ni foam cathode, respectively. The electroreduction via hydrodechlorination (HDC) mechanism involves the reaction of the substance with atomic hydrogen which forms at the cathode surface. Under the tested conditions, the cathodes order of reactivity (Fe<Cu<Ni) is in agreement with electrodes electrocatalytic activity on hydrogen formation. TCE overall removal efficacies achieved with the palladized Fe, Cu, and Ni foam cathodes (0.76 mgPd cm$^{-2}$ geometric area) were 99.8%, 79.6%, and 78.4%, respectively. Normalized pseudo-first-order rate coefficients, $k_{sv}$ (L m$^{2}$ min$^{-1}$) were 7.63x10$^{-4}$, 3.73x10$^{-4}$, and 2.51x10$^{-4}$ for palladized Fe, Cu and Ni foam cathode, respectively. This implies that palladium coating on the cathodes significantly improves their
performance on TCE degradation. The results indicate that cathode material significantly influences TCE degradation efficiency and rate.
THE INFLUENCE OF HUMIC SUBSTANCES ON ELECTROCHEMICAL DEGRADATION OF TRICHLOROETHYLENE BY FE/PD FOAM CATHODE

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Karst aquifers are one of the most susceptible habitat types because of the hydrological connectivity between the surface and subsurface. The surface derived water can carry contaminants and particulate and dissolved organic matter from plant and soil material. In this study, we tested the influence of humic substances (HS) content on electrochemical degradation of trichloroethylene (TCE) from simulated groundwater coming from limestone aquifers. The treatment was conducted by cathode→anode electrode arrangement in the electrochemical flow-through reactor column. Palladized Fe foam was used as the cathode to promote hydrodechlorination of TCE. We used mixed metal oxide (MMO) mesh anode. The final TCE removal percentage was 82.9%, 70.9%, 61.4% and 51.8% when initial HS (measured as total organic carbon content, TOC) was 1 ppm, 2 ppm, 5 ppm and 10 ppm. TOC and DOC values originating from HS as well as DOC/TOC ratio changed during the treatment. As studied in the literature, the reduction of HS appears in the presence of H₂ and Pd catalyst while the electrochemical oxidation can be achieved by MMO anodes. In the system tested, the conditions for mentioned processes occur. It is assumed that reduction and oxidation of HS compete with TCE electrochemical degradation and adversely affect TCE final removal efficacy. Further investigation is needed to confirm and identify the influence of electrochemical treatment on HS structure.
ELECTROKINETIC REMEDIATION OF THE HUMIC URBAN SOILS

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The return of heavy metal ions contaminated humic soils of heavy mechanical composition in the economic turnover is one of the most complicated problems to be solved by using electrokinetic remediation. Electrode processes (the change of acid-alkali balance) and electro-surfacing phenomenon (electroosmos, deformation and polarization DEL) arising under the direct electric current serve as prerequisites to the electrokinetic mass transfer. The double-electric layer (DEL) effect significantly an ion exchange, an adsorption, a host-guest complexation and a mass transfer in the high-dispersity heavy-textured soils. The structural features of the DEL in the humic high-dispersity soils has effect as on a processes of the immobilization and the accumulation of a toxicants, an organic matter, well as on a process of the mass transfer. Volumetric flow rate electrokinetic transporting soils depends on the initial conditions of the electrokinetic tests, mineral composition, dispersity, soil moisture and soil density and chemical composition of pore solution.

There were used the contaminated loamy modified urban soils, not contaminated loam, with varying soil moisture and potassium humate. The method of capillary electrophoresis was used to analyze the cation composition of humates. Electrokinetic tests were conducted in a two-chamber electroosmotic cell. Statistical methods have been used to analyze the results of electrokinetic tests.

The carried studies have established the effect of potassium humate concentration on the distribution of ions near the negatively charged surface of soil minerals at the contaminated loamy
modified urban soils. The value of ζ-potential uniformly decreases as potassium humate concentration increases. Electrokinetic velocity is increased with an increase electrolyte concentration in the pore solution, and then electroosmotic velocity is decreased as compression the diffuse part of double layer.

Electrokinetic tests showed that higher electrokinetic rates observed in pure sandy loam without potassium humate. Apparently, this is due to the fact that humates actively modify the properties and geometry of the pore space urban soils.
ANIONIC SPECIES TRANSPORT THROUGH THE SOIL (ELECTROMIGRATION VERSUS ELECTROOSMOSIS): THE CASE OF EDTA

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The use of EDTA as a complexing agent to extract metals from soil is common. We have tested this possibility for the remediation feasibility studies of a soil contaminated with lead, collected in the mining district of Linares (Spain), a region where the mining activity has been going on for more than 20 centuries.

In this work, we have found that close to 100\% of Pb is removed from the contaminated soil when EDTA is used in batch reactor experiments. However, almost no Pb is removed when EDTA is used as an enhancing agent in electrokinetic soil remediation of the same soil. The percentage of Pb removed is 0-10\% and the analysis of soil after electrokinetic treatment indicates that more than 90\% of Pb remains in the soil. Instead, the use of other mobilization agents that gave also good removal yields for the batch reactor experiments gave also important removals by EKR [1].

Usually it is assumed that the removal of toxic metals during EKR take place by electromigration, which is about one order of magnitude more important than any other transport process, such as electroosmosis, diffusion, etc. [2]. Nevertheless, we found that in EKR experiments enhanced with EDTA, the electroosmotic flow is very important and severely impairs the extraction of lead. The negative charge of the complex is probably the main reason for the different behavior relative to the other mobilization agents.
References


EFFECT OF CAPACITIVE DEIONIZATION ON pH OF SOLUTION

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The results of investigation on sorption and pH variation during charge/discharge cycles for the flow-through capacitive deionization units are presented in the paper. The electrodes for the capacitive deionization units were made from a carbon material SAUT-1C which was modified by titanium. Deposition of titanium coating was made by using the Arc-PVD method. The total volume of the water solution was 1.9 liters, and the circulation flow rate for the solution was around 0.75 L/min. pH was measured by multifunctional device Anion-7051 using the standard method, and the total salt content was controlled by using the conduct meter Bante 950. The programmable low-voltage power supply unit CDS1-5M10 was applied to power the electrochemical unit. The power supply unit includes five individual modules with each having the operating voltage range of -1.8 V ÷ +1.8 V as well as the operating current range of 0-10 A. During the experiment, the capacitive deionization unit was charged in the constant current mode with 5 A DC.

The experiments were carried out in synthetic solutions with concentrations 450, 225 and 175 ppm of NaCl. When the capacitive deionization unit was charged, salt concentration in the output water flow decreased by 8-9 times. pH level, which was measured in a buffer volume, increased during the first minute from 8.05-8.1 up to 8.93-9.43, and then decreased up to 6.7-6.9. The pH growth effect can be explained by the difference in mobility of hydrogen and hydroxyl ion groups by 3 times. Thus, at the first stage, hydrogen ions, hydroxyl groups and ions of dissolved salts are involved in the transfer of current, but the difference in their mobility causes pH growth. At the second stage pH level is decreased as a result of electrochemical processes on the electrodes.
ELECTRICALLY INDUCED PORE PRESSURES AND LIQUID HYDROCARBON OIL TRANSPORT IN SIMULATED COASTAL SOIL DEEP LAYER

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Electrically assisted mass transport of hydrocarbon compounds in natural porous media has been used to recover residual oil from clay rich rock formations. The basic concept in this method builds on the application of direct current (DC) electric field to promote an electro-osmotic flow near the solid-liquid interfaces of water wet-porous media.

In this work, coastal oil pollution where mass transport was induced under a constant DC without supplemental water flooding was simulated in laboratory. Two cells were assembled. One cell with 6 measuring points was assembled with oil, brine water and soil, and the other cell for experimental control was assembled with 8 measuring points and without oil. The pore water pressure (PWP) was measured at 5cm to the bottom of the simulated soil cell at each measuring point.

Results show that the range of voltage fluctuation, for the oil contaminated soil is higher than the soil without oil contaminated, under the same constant DC density. The non-uniform voltage fluctuation gave rise to the fluctuation of PWP; and the fluctuation of PWP near the oil spot was lower than other measuring points of the simulated soil cell.
DESALINATION OF DANISH FARM MASONRY BUILT WITH BRICKS BY ELECTROKINETIC TECHNIQUE

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The soluble salts are considered as the main cause for the damage to the cultural heritage. There are many different techniques which deal with the desalination of the constructions. One of the most interesting is electrokinetic technique. When an electric field is applied into the construction, the ions in the constructions start to move towards the electrodes with the opposite polarity.

The present study shows the possibility of electrokinetics to desalinate a wall of a farm house built in 1950 located in Kongens Lyngby in Denmark. The wall suffered from the salts as high initial concentrations of chlorides, nitrates and sulphates were measured. All of these ions exceeded the limits from ÖNOR.M.B. 3355-1, which advised do an active salt removal.

The main goals of this research are to remove salts from the part of the salt contaminated wall; to find out the removal rates for chlorides, nitrates and sulphates; and to verify whether electro-osmosis (water movement under an applied DC field) takes place between electrodes.

To achieve these objectives a setup consisting of two electrode units filled with the brick clay was performed. The distance between the electrode units was 0.5 m. During the test the voltage was monitored every day. When the voltage increased to the maximum level of a power supply, the clay poultice was changed for a new one. The current was switched off for few days between every change. After every change, the electrode units were filled with the new clay poultice and these were placed exactly on the same position. In addition to the analysis did in the poultices, other analysis was carried out inside the wall before and after the electrokinetic treatment.
The obtained results shows that the chloride, nitrate and sulphate concentrations were reduced efficiently (chloride concentration from 800 ± 510 mg/kg to 450 ± 270 mg/kg; sulphate concentration from 990 ± 1040 mg/kg to 600 ± 550 mg/kg and nitrate concentration from 14420 ± 5440 mg/kg to 9980 ± 950) after 6 months of the desalination treatment.

The removal rate for chloride anions was 0.03 g·day$^{-1}$; nitrate anions 0.4 g·day$^{-1}$ and for sulphate anions 0.05 g·day$^{-1}$. That shows a major part of the charge transfer towards the anode was a nitrate transport. The reduction in the salt concentration could last longer. The used brick clay buffered acidification in the masonry. Electro-osmotic water transport was observed in the clay poultices; however, there was no decrease in the water contents in the masonry at the end of the test.
EVALUATION OF MICROSTRUCTURAL DAMAGE CAUSED BY THE APPLICATION OF ELECTROKINETIC TECHNIQUES IN THE DESALINATION OF DIFFERENT GRANITES

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In recent years, new techniques have emerged to try to combat the problem created by the presence of soluble salts present inside of stone materials. Among these techniques stand out those based on the application of an electric field in order to force the ions to migrate out from architectural facing.

The application of these techniques today generates controversy among the practitioners mainly due to the possible adverse effects that can be generated by their application (damage to the microstructure, new processes of alteration caused by strong changes in pH, etc...).

In this study was evaluated the effectiveness of this technique in the removal of soluble salts present within two granitic substrates contaminated with seawater, it was evaluated also the possible generation of new alteration forms or damage caused by this kind of treatment, with the aim of demonstrate that this fear is unfounded as long as takes place during treatment a number of basic guidelines.

The results obtained in this study show that the application of these techniques can be carried out without any adverse effect which can affect the treated materials. In any case it was appreciated a variation of the physical, mechanical, hydric and textural properties of the treated rocks. Furthermore its application can substantially improve the efficiency and effectiveness of the methods currently used (immersion and the application of poultices), which makes this treatment can be considered as the best solution against this type of alteration agents.
Some outputs of the ELECTROACROSS project
Removal of organic contaminants from soils by an electrokinetic process: The case of molinate and bentazone. Experimental and modeling

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Abstract

The herbicides molinate and bentazone are used in paddy rice fields. Their behaviour in soils when submitted to an electric field was studied and the applicability of the electrokinetic (EK) process in soil remediation was evaluated. Three soils were used and nine EK experiments were carried out at a laboratory scale. A one-dimensional model is developed for simulating the EK treatment of soils containing the herbicides. The model reproduces satisfactorily the experimental data of cumulative volumes removed towards the anode and the cathode compartments, as well as the difference between catholyte and anolyte cumulative volumes, showing that the electroosmotic flow (EOF) is very sensible to soil pH. The experimental results show that the EK process is able to mobilize molinate and bentazone from soils, and remove them from soil solution. Molinate seems to be mobilized preferentially to the cathode compartment. The model also satisfactorily reproduces the experimental data. The highest quantities of molinate move towards the catholyte, particularly when the EOF is kept constant, allowing molinate to be constantly swept towards it. Bentazone also shows a high decay from soil, being mobilized towards both electrode compartments. The results point towards a relationship between the differential pH in the catholyte and anolyte, and the bentazone decay. The model shows that bentazone is mobilized towards the anolyte in higher current intensity conditions, because there is a predominant electromigration (EM) movement of enolate towards the anode compartment, against the electroosmotic transport of bentazone towards cathode, whereas in lower intensity conditions the opposite occurs. This happens because the EOF grows less than EM, when current intensity is duplicated.

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Modeling of electrokinetic processes by finite element integration of the Nernst–Planck–Poisson system of equations

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A B S T R A C T

Electrokinetic remediation covers a variety of useful techniques for the mobilization of ionic and non-ionic species from porous materials by means of the application of an external electric field. Due to the large number of physicochemical interactions in the process, designing an electrokinetic remediation process is not simple. Mathematical models are necessary for a better understanding of its fundamentals.

In this study, a model for the electrokinetic transport phenomena based on the strongly coupled Nernst–Planck–Poisson system of equations is described. In the model presented here, the diffusion, the electromigration and the electroosmotic transport contributors are taken into account. The Poisson’s equation of electrostatics is used for the calculation of the electrical potential distribution based on the global charge balance. The effect of the electrode half-reactions is included. In addition to this, water equilibrium is continuously assured and the pH value is monitored. Results from some selected test simulations of the electrokinetic desalination of a sample of porous material are presented, outlining the versatility of the model as well as showing the effect of the counterion in the removal rate of a target ion.

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Assessing fly ash treatment: Remediation and stabilization of heavy metals

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\section*{Abstract}

Fly ashes from Municipal Solid Waste (MSW), straw (ST) and co-combustion of wood (CW) are here analyzed with the intent of reusing them. Two techniques are assessed, a remediation technique and a solidification/stabilization one. The removal of heavy metals from fly ashes through the electrodialytic process (EDR) has been tried out before. The goal of removing heavy metals has always been the reuse of fly ash, for instance in agricultural fields (BEK). The best removal rates are here summarized and some new results have been added. MSW fly ashes are still too hazardous after treatment to even consider application to the soil. ST ash is the only residue that gets concentrations low enough to be reused, but its fertilizing value might be questioned. An alternative reuse for the three ashes is here preliminary tested, the combination of fly ash with mortar. Fly ashes have been substituted by cement fraction or aggregate fraction. Surprisingly, better compressive strengths were obtained by replacing the aggregate fraction. CW ashes presented promising results for the substitution of aggregate in mortar and possibly in concrete.

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Review

Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies

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ABSTRACT

Electrokinetic remediation has been increasingly used in soils and other matrices for numerous contaminants such as inorganic, organic, radionuclides, explosives and their mixtures. Several strategies were tested to improve this technology effectiveness, namely techniques to solubilize contaminants, control soil pH and also couple electrokinetics with other remediation technologies. This review focus in the experimental work carried out in organochlorines soil electroremediation, aiming to systematize useful information to researchers in this field. It is not possible to clearly state what technique is the best, since experimental approaches and targeted contaminants are different. Further research is needed in the application of some of the reviewed techniques. Also a number of technical and environmental issues will require evaluation for full-scale application. Removal efficiencies reported in real contaminated soils are much lower than the ones obtained with spiked kaolinite, showing the influence of other factors like aging of the contamination and adsorption to soil particles, resulting in important challenges when transferring technologies into the field.

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Electrokinetic Enhanced Transport of Zero Valent Iron Nanoparticles for Chromium(VI) Reduction in Soils

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Zero valent iron nanoparticles (nZVI) are a promising technology that could provide cost-effective solutions to soil and groundwater remediation. However, transport of nZVI is normally limited by their aggregation and settling, and with mobility being normally less than a few meters. The main research objective of this study is to find out if coupling electrokinetics and reactive iron nanoparticles can be an effective method for treating chromium contaminated clay soils. Direct current was used to enhance poly(acrylic acid), sodium salt (PAA) coated iron nanoparticles (PAA-nZVI) mobility in Cr(VI) spiked kaolin. A commercially available electrophoretic cell was modified for these experiments and equipped with internal auxiliary electrodes that allow to measure the redox potential directly in the clay. A constant potential of 5.0 V was applied across the test bed. Experimental results show that electrokinetics can enhance the delivery of nanoscale iron particles for the reduction of hexavalent chromium to the less toxic trivalent chromium. Direct current enhanced nZVI transport up to 74 % when compared with diffusion, maximum value found when comparing iron concentrations ratios. Activation of nZVI was also observed with a decrease in the redox potential of 531 mV, in average, after the injection point.
Electrodialytic Remediation of heavy Metal polluted Soil – treatment of water saturated or suspended soil

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Electrodialytic soil remediation is a method for removal of heavy metals. Good results have previously been obtained with both treatment of a stationary, water saturated soil matrix and with remediation of a stirred suspension of soil in water. The two different setups have different uses. The first as in-situ or on-site treatment when there is no requirement for fast remediation, as the removal rate of the heavy metals are dependent on the distance between the electrodes (everything else equal) and in such application the electrode spacing must have a certain distance (often meters). In the stirred setup it is possible to shorten the transport route to few mm and to have a faster and continuous process. The present paper for the first time reports a direct comparison of the two options. The remediation of the stirred suspension showed faster than remediation of the water saturated soil even without a short distance between the membranes. The acidification of the suspended soil was fastest and following the mobilization of heavy metals. This may indicate that water splitting at the anion exchange membrane is used more efficiently in the stirred setup.
Modeling of electrokinetic desalination of bricks

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\textbf{Abstract}

A model for the reactive transport of matter through porous media induced by an externally applied electric field is discussed. The Nernst–Planck–Poisson system of equations is used for modeling multispecies electro-diffusion transport phenomena, assuming chemical equilibrium during the process. The system of equations includes the transport of water and the resulting advective flow of the aqueous species. The model takes into account transient change in porosity and its impact on transport. Test examples were performed and compared to experimental data for electrokinetic desalination treatment of yellow bricks contaminated with chloride salts.

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Simulation-based analysis of the differences in the removal rate of chlorides, nitrates and sulfates by electrokinetic desalination treatments

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ABSTRACT

Due to their abundance in the natural environment, chloride, nitrate and sulfate salts are considered the main responsible for the salt-induced decay processes in building materials and sculptures. Electro-desalination techniques, enhanced with carbonated clay buffer poultice placed between the surface of the stone and the electrodes, have been successfully applied for the prevention of salt-induced deterioration problems of masonry and other construction materials. However, it has been experimentally observed that, in this type of treatments, the removal rate of sulfates is considerably slower than chlorides and nitrates.

A physicochemical model for electrochemically induced reactive-transport processes is described and used for a theoretical analysis of the influence of the chemical interactions on the removal rate of the target ions. Simulations for the electro-desalination of a brick sample contaminated with a combination of these target ions are shown. Results from simulations show that the lower removal efficiency of sulfates is related to the precipitation of gypsum inside the porous body. Modifications of the existing technique are suggested based on the simulation results.

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Review

Overview of in situ and ex situ remediation technologies for PCB-contaminated soils and sediments and obstacles for full-scale application

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\textbf{HIGHLIGHTS}

- Remediation technologies for PCB in contaminated soils and sediments
- Review of in situ and ex situ remediation technologies
- Historical overview of full-scale applications for PCB contaminated sites
- Assessment of full-scale applications of emerging technologies

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\textbf{ABSTRACT}

Polychlorinated biphenyls (PCB) are persistent organic pollutants used worldwide between the 1930s and 1980s. Although their use has been heavily restricted, PCB can be found in contaminated soils and sediments. The most frequent remediation solutions adopted are “dig and dump” and “dig and incinerate”, but there are currently new methods that could be more sustainable alternatives. This paper takes a look into the remediation options available for PCB-contaminated soils and sediments, differentiating between biological, chemical, physical and thermal methods. The use of combined technologies was also reviewed. Most of them are still in an initial development stage and further research in different implementation issues is needed. There is no single technology that is the solution for PCB contamination problem. The successful remediation of a site will depend on proper selection, design and adjustment of the technology or combined technologies to the site characteristics.
Phosphorus Recovery from a Water Reservoir—Potential of Nanofiltration Coupled to Electrodialytic Process

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Abstract Worldwide waste streams can represent an environmental problem if they are considered “deleterious material”. These streams may also be a source of secondary resources when enclosing compounds with potential to be recovered. Phosphorus (P) is one of those, with an increasing interest, as it is essential for life but its non-renewable reserves are expected to last about one century. Nanofiltration (NF) and electrodialytic process (ED) were applied to a stream from a Water Treatment Plant (WTP). Water from Funcho Dam Reservoir, Portugal, was subject of NF treatment followed by ED process for P recovery. The feed concentration of P for ED process was between 1,429 and 1,845 µg/L. Optimization studies were carried out in laboratory cells. Almost complete P removal out of the central compartment of the ED cell was observed under the action of an applied electric field. Experiments lasted between ca. 7 and 42 h experimental-period, depending on concentrate parameters. In less than 7 h of ED, 72 % of P was recovered in the anolyte and thereby separated from the concentrate stream. Nanofiltration coupled to ED can be considered a promising and sustainable technology to upgrade waste streams, recovering P and avoiding the intensive mining of phosphate rock.

Keywords Phosphorus · Electrokinetic recovery · Nanofiltration · Membrane concentrate · Waste valorisation
Computing multi-species chemical equilibrium with an algorithm based on the reaction extents

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A mathematical model for the solution of a set of chemical equilibrium equations in a multi-species and multiphase chemical system is described. The computer-aid solution of model is achieved by means of a Newton–Raphson method enhanced with a line-search scheme, which deals with the non-negative constrains. The residual function, representing the distance to the equilibrium, is defined from the chemical potential (or Gibbs energy) of the chemical system. Local minimums are potentially avoided by the prioritization of the aqueous reactions with respect to the heterogeneous reactions. The formation and release of gas bubbles is taken into account in the model, limiting the concentration of volatile aqueous species to a maximum value, given by the gas solubility constant.

The reaction extents are used as state variables for the numerical method. As a result, the accepted solution satisfies the charge and mass balance equations and the model is fully compatible with general reactive transport models.

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Surfactants-enhanced electrokinetic transport of xanthan gum stabilized nanoPd/Fe for the remediation of PCBs contaminated soils

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Soil remediation

\textbf{Abstract}

Polychlorinated biphenyls (PCBs) in the environment pose long-term risk to public health because of their persistence and toxicity. In this study, a novel technology called EK + nano (electrokinetic technology combined with engineered nanoparticles) was used to remediate polychlorinated biphenyls (PCBs) contaminated soil. Three different surfactants (anionic surfactant – SDBS, nonionic surfactant – Brij35 and biosurfactant – rhamnolipid) for enhancing the solubilization of soil PCBs were applied separately with xanthan gum stabilized nanoPd/Fe. The stabilized nanoPd/Fe was injected in the compartment located 3 cm from the anode chamber daily in EK tests. The results indicated that the surfactants addition enhanced the solubilization capacity of PCB28 significantly but did not affect the stability of xanthan gum–nanoPd/Fe suspension. The nanoparticles were successfully transported along with the soil column by EK, and apparent increase of Fe content was found toward the cathode. Higher electroosmotic flow favored the migration of nanoparticles, but the degradation was limited without addition of surfactant. Brij35–xanthan gum stabilized nanoPd/Fe gave the highest removal efficiency of PCBs, both in batch experiments and EK tests, in which the removal rates of approximately 50% and 20% were achieved, respectively. The functions of SDBS and rhamnolipid in soil PCBs removal were not significant in all tests.

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Suitability of oil bioremediation in an Artic soil using surplus heating from an incineration facility

Nazaré Couto · Janne Fritt-Rasmussen · Pernille E. Jensen · Mads Højrup · Ana P. Rodrigo · Alexandra B. Ribeiro

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Abstract A 168-day period field study, carried out in Sisimiut, Greenland, assessed the potential to enhance soil remediation with the surplus heating from an incineration facility. This approach searches a feasible ex situ remediation process that could be extended throughout the year with low costs. Individual and synergistic effects of biostimulation were also tested, in parallel. An interim evaluation at the end of the first 42 days showed that biostimulation and active heating, as separate treatments, enhanced petroleum hydrocarbon (PHC) removal compared to natural attenuation. The coupling of both technologies was even more effective, corroborating the benefits of both techniques in a remediation strategy. However, between day 42 and day 168, there was an opposite remediation trend with all treatments suggesting a stabilization except for natural attenuation, where PHC values continued to decrease. This enforces the “self-purification” capacity of the system, even at low temperatures. Coupling biostimulation with active heating was the best approach for PHC removal, namely for a short period of time (42 days). The proposed remediation scheme can be considered a reliable option for faster PHC removal with low maintenance and using “waste heating” from an incineration facility.

Keywords Arctic · Bioremediation · Biostimulation · Oil contamination · Surplus heat
Influence of electrolyte and voltage on the direct current enhanced transport of iron nanoparticles in clay

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HIGHLIGHTS

- Direct current can enhance iron nanoparticles transport in clay by 25%.
- Oxidizing conditions and higher ionic strength limit nZVI enhanced transport.
- Ionic strength was significant, promoting nanoparticles aggregation and oxidation.

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ABSTRACT

Zero valent iron nanoparticles (nZVI) transport for soil and groundwater remediation is slowed down or halted by aggregation or fast depletion in the soil pores. Direct electric current can enhance the transport of nZVI in low permeability soils. However, operational factors, including pH, oxidation–reduction potential (ORP), voltage and ionic strength of the electrolyte can play an important role in the treatment effectiveness. Experiments were conducted to enhance polymer coated nZVI mobility in a model low permeability soil medium (kaolin clay) using low direct current. Different electrolytes of varying ionic strengths and initial pH and high nZVI concentrations were applied. Results showed that the nZVI transport is enhanced by direct current, even considering concentrations typical of field application that favor nanoparticle aggregation. However, the factors considered (pH, ORP, voltage and electrolyte) failed to explain the iron concentration variation. The electrolyte and its ionic strength proved to be significant for pH and ORP measured during the experiments, and therefore will affect aggregation and fast oxidation of the particles.

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Phosphorus recovery from sewage sludge ash through an electrodialytic process

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The electrodialytic separation process (ED) was applied to sewage sludge ash (SSA) aiming at phosphorus (P) recovery. As the SSA may have high heavy metals contents, their removal was also assessed. Two SSA were sampled, one immediately after incineration (SA) and the other from an open deposit (SB). Both samples were ED treated as stirred suspensions in sulphuric acid for 3, 7 and 14 days. After 14 days, phosphorus was mainly mobilized towards the anode end (approx. 60% in the SA and 70% in the SB), whereas heavy metals mainly electromigrated towards the cathode end. The anolyte presented a composition of 98% of P, mainly as orthophosphate, and 2% of heavy metals. The highest heavy metal removal was achieved for Cu (ca. 80%) and the lowest for Pb and Fe (between 4% and 6%). The ED showed to be a viable method for phosphorus recovery from SSA, as it promotes the separation of P from the heavy metals.

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Electrokinetic remediation of six emerging organic contaminants from soil

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HIGHLIGHTS

- Electrokinetic remediation is a viable method for organic contaminants removal.
- Between 50% and 80% of the contaminants were remediated after four days.
- Electroosmosis was the main mechanism responsible for contaminants mobilization.
- Electrodegradation should also be taken into account in this remediation process.

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ABSTRACT

Some organic contaminants can accumulate in organisms and cause irreversible damages in biological systems through direct or indirect toxic effects. In this study, the feasibility of the electrokinetic (EK) process for the remediation of 17β-oestradiol (E2), 17α-ethinylestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), octylphenol (OP) and triclosan (TCS) in soils was studied in a stationary laboratory cell. The experiments were conducted using a silty loam soil (S2) at 0, 10 and 20 mA and a sandy soil (S3) at 0 and 10 mA. A pH control in the anolyte reservoir (pH > 13) at 10 mA was carried out using S2, too. Photo and electrodegradation experiments were also fulfilled. Results showed that EK is a viable method for the remediation of these contaminants, both through mobilization by electroosmotic flow (EOF) and electrodegradation. As EOF is very sensible to soil pH, the control in the anolyte increased EOF rate, consequently enhancing contaminants mobilization towards the cathode end. The extent of the mobilization towards the electrode end was mainly dependent on compounds solubility and octanol-water partition coefficient. In the last 24 h of experiments, BPA presented the highest mobilization rate (ca. 4 μg min⁻¹) with NP not being detected in the catholyte. At the end of all experiments the percentage of contaminants that remained in the soil ranged between 17 and 50 for S2, and between 27 and 48 for S3, with no statistical differences between treatments. The mass balance performed showed that the amount of contaminant not detected in the cell is similar to the quantity that potentially may suffer photo and electrodegradation.

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Phosphorus recovery from waters using nanofiltration

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\textbf{ABSTRACT}

Recovery of phosphorus has been gaining importance due to its natural scarcity and expensive price. In this work, nanofiltration (NF) has been tested as a technology to treat surface waters with phosphorus and simultaneously recover that phosphorus. Two membranes of same material, but different molecular size were tested (NF270 and NF90). Results showed that membrane fluxes were more affected by the presence of salts, natural organic matter, and especially microcystins than phosphorus. In addition, phosphorus removals were very high (>90\%) and varied with the membrane type, feed conductivity, and dissolved organic carbon (DOC). The increase in feed conductivity and DOC originated higher phosphorus removals. Furthermore, the presence of microcystins did not affect the high-phosphorus removals. Results show that more than 96\% of the total phosphorus mass can be recovered using NF membranes. NF is therefore a technology that should be considered for phosphorus recovery from surface waters.

\textit{Keywords:} Phosphorus; Recovery; Removal; Nanofiltration; Surface waters
Assessment of combined electro-nanoremediation of molinate contaminated soil

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HIGHLIGHTS

• Molinate is degraded in soil by zero valent iron nanoparticles (nZVI).
• Higher contact time of nZVI with soil facilitates molinate degradation.
• Soil type was the most significant factor influencing iron and molinate transport.
• When using nZVI and EK molinate is not only transported to catholyte, but also degraded.

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ABSTRACT

Molinate is a pesticide widely used, both in space and time, for weed control in rice paddies. Due to its water solubility and affinity to organic matter, it is a contaminant of concern in ground and surface waters, soils and sediments. Previous works have showed that molinate can be removed from soils through electrokinetic (EK) remediation.

In this work, molinate degradation by zero valent iron nanoparticles (nZVI) was tested in soils for the first time. Soil is a highly complex matrix, and pollutant partitioning between soil and water and its degradation rates in different matrices is quite challenging. A system combining nZVI and EK was also set up in order to study the nanoparticles and molinate transport, as well as molinate degradation.

Results showed that molinate could be degraded by nZVI in soils, even though the process is more time demanding and degradation percentages are lower than in an aqueous solution. This shows the importance of testing contaminant degradation, not only in aqueous solutions, but also in the soil-sorbed fraction. It was also found that soil type was the most significant factor influencing iron and molinate transport. The main advantage of the simultaneous use of both methods is the molinate degradation instead of its accumulation in the catholyte.

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