Contents

Welcome .................................................................................................................. 7
Organizing and Scientific Committees ................................................................. 8
Scientific and Social Programme ..................................................................... 11
Oral presentations .............................................................................................. 19
Poster presentations ......................................................................................... 111
Index of authors ................................................................................................. 251
Practical information ........................................................................................ 255
Notes ..................................................................................................................... 256
Location maps .................................................................................................. 266
Welcome

On behalf of the Organizing Committee, we warmly welcome you to the 2016 Interfaces Against Pollution conference (IAP 2016) that will be held in the modern “Transfronterer building”, in Lleida (Catalonia, Spain) from Sunday 4th September to Wednesday 7th September 2016.

This 9th edition of the International Conference on Interfaces Against Pollution continues the series of conferences initiated in Wageningen (The Netherlands, 1997), and followed by Miskolc (Hungary, 2002), Jülich (Germany, 2004), Granada (Spain, 2006), Kyoto (Japan, 2008), Beijing (China, 2010), Nancy (France, 2012) and Leeuwarden (Netherlands, 2014).

The Interfaces Against Pollution series of conferences is devoted to the understanding of those phenomena relating colloids and interfaces with pollutants in environmental media. The current situation of our planet makes Environmental Science and Technology one of the central fields of research to achieve a sustainable development of humanity. The impact of anthropogenic activity brings up a number of potentially adverse effects on the environment, which pose many challenges for researchers around the world. On the other hand, a deep insight into the physicochemical mechanisms involved in the fate and behaviour of pollutants in environmental compartments represents many opportunities for Research, Development and Innovation of novel monitoring tools, predictive models for the risk assessment of current and emerging substances, technologies for remediation of contaminants, etc. which will be helpful for the sustainable development of chemical industries in the near future.

We sincerely hope that this Conference will be an opportunity for researchers working in the field of environmental surface and colloid science to get together in a friendly and constructive atmosphere in Lleida.

Jaume Puy (Chair)
P.I. Group of Environmental Physical Chemistry
Vice-rector of Research, Universitat de Lleida

Josep Galceran, Carlos Rey-Castro (co-Chairs)
Organizing and Scientific Committees

Chair of the IAP International Advisory Council

T. David Waite
University of New South Wales, Australia

Past president and Founder of IAP

Luuk K. Koopal
Wageningen University, The Netherlands

IAP International Advisory Committee

Yasuhisa Adachi (Japan)
Marcelo Avena (Argentina)
Philippe Behra (France)
Maarten Biesheuvel (Netherlands)
Andrzej Dabrowski (Poland)
Jerome Duval (France)
Menachim Elimelech (USA)
Ellen Graber (Israel)
Bert Hamelers (Netherlands)
Hong He (China)
Munehide Ishiguro (Japan)
Erwin Klump (Germany)
Luuk Koopal (Netherlands)
Gianluca Li Puma (UK)
Yael Mishael (Israel)
Nataliya Mishchuk (Ukraine)
Jaume Puy (Spain)
Jiuhui Qu (China)
Michael Sander (Switzerland)
Etelka Tombacz (Hungary)
Raewyn Town (Denmark)
Paul Tratnyek (USA)
David Waite (Australia)
Kevin Wilkinson (Canada)
International Scientific Committee IAP2016

Yasuhisa Adachi (Japan)
Maarten Biesheuvel (Netherlands)
Jerome Duval (France)
Josep Galceran (Spain)
Jaume Puy (Spain, chair)
Carlos Rey-Castro (Spain)
Raewyn Town (Denmark)
David Waite (Australia)

Local organizing Committee IAP2016

Jaume Puy (Chair)
Josep Galceran (Co-chair)
Carlos Rey-Castro (Co-chair)
Francesc Mas, Univ. Barcelona
Encarna Companys
Joan Cecilia
Josep Monné
Calin David
# Programme at a glance

## Scientific and Social Programme

### Sunday, September 4th, 2016

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>19:00-21:00</td>
<td>Welcome cocktail and Registration</td>
<td>Rectorat Universitat de Lleida</td>
</tr>
<tr>
<td></td>
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<td>Plaça Víctor Siurana 1</td>
</tr>
</tbody>
</table>

### Monday, September 5th, 2016

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:15-18:00</td>
<td>Registration</td>
<td>Transfronterer Building</td>
</tr>
<tr>
<td>8:45-9:00</td>
<td>Opening Ceremony</td>
<td>Auditorium</td>
</tr>
<tr>
<td>9:00-10:40</td>
<td>Plenary Lectures</td>
<td>Auditorium</td>
</tr>
<tr>
<td>10:40-11:10</td>
<td>Fruit &amp; coffee break</td>
<td>Multipurpose building</td>
</tr>
<tr>
<td>11:10-12:30</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
</tr>
<tr>
<td>12:30-14:00</td>
<td>Lunch</td>
<td>Multipurpose building</td>
</tr>
<tr>
<td>14:00-15:20</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
</tr>
<tr>
<td>15:20-15:40</td>
<td>Fruit &amp; coffee break</td>
<td>Multipurpose building</td>
</tr>
<tr>
<td>15:40-17:00</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
</tr>
<tr>
<td>17:00-18:00</td>
<td>Poster session &amp; networking</td>
<td>Below auditorium hall</td>
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<tr>
<td></td>
<td></td>
<td>(with drinks and snacks)</td>
</tr>
<tr>
<td>19:30-22:00</td>
<td>Visit to La Seu; buses departure in front of Auditorium building at 19:15</td>
<td>Auditorium</td>
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<tr>
<td></td>
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<td>(food and refreshments will be served)</td>
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</tbody>
</table>

### Tuesday, September 6th, 2016

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
<th>Location</th>
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<tbody>
<tr>
<td>9:00-10:40</td>
<td>Plenary Lectures</td>
<td>Auditorium</td>
</tr>
<tr>
<td>10:40-11:10</td>
<td>Fruit &amp; coffee break</td>
<td>Multipurpose building</td>
</tr>
<tr>
<td>11:10-12:30</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
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<tr>
<td>12:30-14:00</td>
<td>Lunch</td>
<td>Multipurpose building</td>
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<tr>
<td></td>
<td>(IAP Board Meeting, room 2.13)</td>
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<tr>
<td>14:00-15:20</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
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<tr>
<td>15:20-15:40</td>
<td>Fruit &amp; coffee break</td>
<td>Multipurpose building</td>
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<tr>
<td>15:40-17:00</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
</tr>
<tr>
<td>17:00-18:00</td>
<td>Poster session &amp; networking</td>
<td>Below auditorium hall</td>
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<tr>
<td></td>
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<td>(with drinks and snacks)</td>
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<tr>
<td>20:30-22:00</td>
<td>Gala Dinner</td>
<td>Restaurant El Mirador</td>
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<td>Av. President Josep Tarradellas, 45</td>
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<td>(walking distance of the Auditorium)</td>
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<tr>
<td>Time</td>
<td>Event</td>
<td>Location</td>
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<tr>
<td>9:00-10:40</td>
<td>Plenary Lectures</td>
<td>Auditorium</td>
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<tr>
<td>10:40-11:10</td>
<td>Fruit &amp; coffee break</td>
<td>Multipurpose building</td>
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<tr>
<td>11:10-12:50</td>
<td>Parallel sessions</td>
<td>Law and Economy Faculty</td>
</tr>
<tr>
<td>13:00-13:20</td>
<td>Closing Ceremony, Awards</td>
<td>Auditorium</td>
</tr>
<tr>
<td>13:20-15:00</td>
<td>Lunch</td>
<td>Multipurpose building</td>
</tr>
<tr>
<td>15:00-19:00</td>
<td>Tutorial on Capacitive Deionization (registration needed)</td>
<td>Computer room 1.08 in multipurpose building (above cafeteria)</td>
</tr>
<tr>
<td>Time</td>
<td>Event</td>
<td>Speaker/Description</td>
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<tr>
<td>8:15 AM</td>
<td>Registration (Transfronterer Building)</td>
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</tr>
<tr>
<td>8:45 AM</td>
<td>Opening Ceremony (Auditorium Room)</td>
<td></td>
</tr>
<tr>
<td>9:00 AM</td>
<td><strong>Susan L.S. Stipp</strong> (OM01 P, p.20) Interfaces Against Pollution: Learning from nature to meet society’s challenges</td>
<td></td>
</tr>
<tr>
<td>9:50 AM</td>
<td><strong>Kenneth A. Dawson</strong> (OM02 P, p.21) New Frontier of Bio-Nano Interactions</td>
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<tr>
<td>10:40 AM</td>
<td>Fruit &amp; coffee break</td>
<td></td>
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<tr>
<td>11:10 AM</td>
<td><strong>Session 1 Room A</strong></td>
<td></td>
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<tr>
<td></td>
<td>Session 1 Room A Environmental impact of nanomaterials I Chair: K.A. Dawson</td>
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<td></td>
<td><strong>Session 1 Room B</strong></td>
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<tr>
<td></td>
<td>Session 1 Room B Biogeochemical cycles I Chair: S.L.S. Stipp</td>
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<td></td>
<td><strong>Session 1 Room C</strong></td>
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<tr>
<td></td>
<td>Session 1 Room C Interfaces for Environmental applications I Chair: M.A. Anderson</td>
<td></td>
</tr>
<tr>
<td>11:10 AM</td>
<td><strong>J.R. Lead:</strong> Manufactured nanoparticles in natural systems; some uses and questions (OM03 KN, p.22)</td>
<td></td>
</tr>
<tr>
<td>11:30 AM</td>
<td><strong>K. Danielsson:</strong> Influence of Natural Organic Matter Model Molecules on the Aggregation of TiO₂ Nanoparticles (OM04, p.23)</td>
<td></td>
</tr>
<tr>
<td>11:50 AM</td>
<td><strong>L. Gutierrez:</strong> Natural Organic matter interfacial interactions with tannic acid-coated Silver nanoparticles: Implications on nanocontaminants mobility (OM05, p.24)</td>
<td></td>
</tr>
<tr>
<td>12:10 PM</td>
<td><strong>W. Sun:</strong> Sediments inhibit 17β-estradiol and 17α-ethinylestradiol adsorption by carbon nanotubes and graphene oxide. Effects of sediment particle size and organic matters (OM06, p.25)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>M.F. Benedetti:</strong> Organic matter dynamics in the Amazon river basin (OM15 KN, p.34)</td>
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<td></td>
<td><strong>P.J.J. Alvarez:</strong> Nanotechnology-Enabled Water Treatment: A Vision to Enable Decentralized Water Treatment and Reuse (OM27 KN, p.46)</td>
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<td></td>
<td><strong>M. Borisover:</strong> Sorbed organic compound induces hydration of natural organic matter (NOM): A cooperative NOM swelling or a condensation in NOM environment? (OM16, p.35)</td>
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<td><strong>C. Lomenech:</strong> Water purification using oleate-modified magnetic nanoparticles (OM28, p.47)</td>
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<td><strong>K. Palanivelu:</strong> Leaching studies on marine shells using carbonated sea water (OM17, p.36)</td>
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<td></td>
<td><strong>S.G. Muntean:</strong> Removal of organic pollutants from wastewaters by magnetite/ carbon nanocomposites (OM29, p.48)</td>
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<td></td>
<td><strong>L.H.E. Winkel:</strong> The global biogeochemical cycle of selenium (OM18 KN, p.37)</td>
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</table>
## Scientific and Social Programme

### Monday 5th September

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 2 Room A</th>
<th>Session 2 Room B</th>
<th>Session 2 Room C</th>
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<tbody>
<tr>
<td>12:30 PM</td>
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<tr>
<td>LUNCH</td>
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<tr>
<td>02:00 PM</td>
<td><strong>J. Rose:</strong> Physical-chemical state and mechanisms of nanomaterial release from products during their life cycle: ageing effects at the products interfaces (OM07 KN, p.26)</td>
<td><strong>R.M. Town:</strong> Intraparticulate metal speciation analysis: electrostatic and covalent contributions to binding of Cd²⁺, Pb²⁺ and Cu²⁺ by humic acid nanoparticles (OM19 KN, p.38)</td>
<td><strong>N. Tufenkji:</strong> Green synthesis of ultra-strong nanocomposite hydrogels for water treatment (OM30 KN, p.49)</td>
</tr>
<tr>
<td>02:20 PM</td>
<td><strong>K.N.M. Mahdi:</strong> Silver nanoparticles in soil: aqueous extraction combined with single-particle ICP-MS for detection and characterization (OM08, p.27)</td>
<td><strong>V. Bolaños:</strong> Isotopically exchangeable pool of Cr (E&lt;sub&gt;Cr&lt;/sub&gt; value) in surface water: the colloidal contribution (OM20, p.39)</td>
<td><strong>L. Duclaux:</strong> Adsorption of ibuprofen on a microporous carbon fabric, effect of ultrasound irradiation, competition with organic matter, and pore filling by a biofilm (OM31, p.50)</td>
</tr>
<tr>
<td>02:40 PM</td>
<td><strong>A. Praetorius:</strong> Single-particle element fingerprints for the detection of engineered cerium oxide nanoparticles in soils (OM09, p.28)</td>
<td><strong>C. Parat:</strong> ISIDORE probe for trace metal speciation: from equilibrium to dynamic approach (OM21, p.40)</td>
<td><strong>T.D. Pham:</strong> Adsorptive removal of organic and inorganic pollutants from aqueous solution by surfactant modified alumina (OM32, p.51)</td>
</tr>
<tr>
<td>03:00 PM</td>
<td><strong>K.A. Jensen:</strong> Screening and ranking of the redox and acid-base reactivity during transformation and dissolution of manufactured nanomaterials in hydrous mediums: Valuable information for risk assessment? (OM10 KN, p.29)</td>
<td><strong>J.P. Pinheiro:</strong> Addressing temperature effects on metal chemodynamics (OM22 KN, p.41)</td>
<td><strong>R.K. Dey:</strong> Study of kinetics, thermodynamics and mechanism of defluoridation of drinking water using metal-loaded polymers (OM33, p.52)</td>
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</table>
## Scientific and Social Programme

### Monday 5th September

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 3 Room A</th>
<th>Session 3 Room B</th>
<th>Session 3 Room C</th>
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<tbody>
<tr>
<td>03:20 PM</td>
<td>Fruit &amp; coffee break</td>
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<tr>
<td>03:40 PM</td>
<td><strong>Environmental impact of nanomaterials III</strong>&lt;br&gt;Chair: J.Rose</td>
<td><strong>Metal-humic interactions</strong>&lt;br&gt;Chair: M.F. Benedetti</td>
<td><strong>Interfaces for Environmental applications III</strong>&lt;br&gt;Chair: N. Tufenkji</td>
</tr>
<tr>
<td>04:00 PM</td>
<td><strong>R. Behra:</strong> Interactions of nanoparticles with four fresh water algal strains (OM11 KN, p.30)</td>
<td><strong>T. Saito:</strong> Ion-binding properties of humic substance in deep sedimentary groundwater (OM23 KN, p.42)</td>
<td><strong>M. A. Anderson:</strong> Building a Better Environment by Doing Things “Porely” (OM34 KN, p.53)</td>
</tr>
<tr>
<td>04:20 PM</td>
<td><strong>A. Anderson:</strong> Transport of waste-generated metallic colloids and nanoparticles in the Environment (OM12, p.31)</td>
<td><strong>W. Chen:</strong> Dependency of Pb, Cd, and Zn binding on sources of dissolved organic matter (OM24, p.43)</td>
<td><strong>A. Tiraferri:</strong> Water Chemistry Affects the Efficacy of Concentrated Suspensions of Iron Oxide Nanoparticles Used for Aquifer Reclamation (OM35, p.54)</td>
</tr>
<tr>
<td>04:40 PM</td>
<td><strong>R.F. Domingos:</strong> A Kinetic Environmental Fate Model for the Risk Assessment of Engineered Nanomaterials (OM13, p.32)</td>
<td><strong>J.E. Groenenberg:</strong> Modelling of tri-valent metal binding to humic substances with the NICA-Donnan model (OM25, p.44)</td>
<td><strong>Y. Hu:</strong> Synthesis of Mg(OH)$_2$-coated nanoscale zero-valent iron (NZVI) for improved mobility and in-situ remediation in sand columns (OM36, p.55)</td>
</tr>
<tr>
<td>05:00 PM</td>
<td><strong>N. Hondow:</strong> Quantitative electron microscopy to probe nanoparticle dispersions and cellular uptake (OM14 KN, p.33)</td>
<td><strong>J. Xu:</strong> Copper Binding to Soil Fulvic and Humic Acids: NICA-Donnan Modeling and Conditional Affinity Spectra (OM26, p.45)</td>
<td><strong>K. Saeed:</strong> Preparation, Characterization and Applications of Electrospun Polyacrylonitrile Nanofibers (OM37, p.56)</td>
</tr>
<tr>
<td>05:00 PM</td>
<td><strong>Poster session &amp; networking</strong>&lt;br&gt;with drinks and snacks</td>
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<tr>
<td>07:30 PM</td>
<td><strong>Social event:</strong> visit to La Seu Vella, with food and refreshments</td>
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</table>
## Tuesday 6th September

### 9:00 AM
**Francois M.M. Morel** (OT01 P, p.57)  
Strong and weak chelators conspire to control the bioavailability of trace metals to microbes

### 9:50 AM
**Peter G.C. Campbell** (OT02 P, p.58)  
Influence of interfacial phenomena on metal uptake by aquatic organisms

### 10:40 AM  
Fruit & coffee break

<table>
<thead>
<tr>
<th>Session 4 Room A</th>
<th>Session 4 Room B</th>
<th>Session 4 Room C</th>
</tr>
</thead>
</table>
| **Metal-bio interactions**  
Chair: P.G.C. Campbell | **Interfacial phenomena: theory & modelling**  
Chair: A. V. Delgado | **Interfaces for Environmental applications IV**  
Chair: T.D. Waite |

### 11:10 AM
**V.I. Slaveykova**: Mercury species bioavailability to aquatic primary producers: from the cell to the community level (OT03 KN, p.59)  
**J.F. Dufrêche**: Multiscale modelling for decontamination of aqueous solution using porous oxides (OT14 KN, p.70)  
**E. Brillas**: Electrochemical advanced oxidation processes: Application to the remediation of waters with organic pollutants (OT26 KN, p.82)

### 11:30 AM
**F.A.R. Barbosa**: Cyanobacteria is resistant to Hg and useful for its removal from aqueous medium (OT04, p.60)  
**M. Predota**: The molecular origin of zeta-potentials as revealed by non-equilibrium molecular dynamics simulations of a realistic mineral-aqueous solution interface (OT15, p.71)  
**A. D’Haese**: Transport of OMPs through FO membranes: influence of OMP and draw solute properties (OT27, p.83)

### 11:50 AM
**J.F.L. Duval**: Kinetic and thermodynamic determinants of metal partitioning at bionterfaces: impacts of intracellular speciation dynamics (OT05, p.61)  
**T. Preocanin**: Inner surface potential measurements and interpretation of equilibrium at electrical interfacial layer (OT16, p.72)  
**M. Stefanescu**: Hybrid sonolysis application as polishing step for removal of THMs generated from the drinking water treatment flow based on coagulation-flocculation, filtration and chlorination (OT28, p.84)

### 12:10 PM
**Y. Adachi**: Dynamics of water soluble polyelectrolytes at the occasion of adsorption on the surface of colloidal particles probed by flocculation properties (OT17 KN, p.73)  
**R. Prasad**: Catalysis and kinetics of diesel soot oxidation over nano-size perovskite catalyst (OT29, p.85)

### 12:30 PM  
LUNCH

<table>
<thead>
<tr>
<th>Session 5 Room A</th>
<th>Session 5 Room B</th>
<th>Session 5 Room C</th>
</tr>
</thead>
</table>
| **Soils and sediments I**  
Chair: L.K. Koopal | **Analytical techniques I**  
Chair: R. M. Town | **Interfaces for Environmental applications V**  
Chair: E. Brillas |

### 02:00 PM
**L. Weng**: Modelling Adsorption Processes at the Interfaces of Soil Particles - 15 Years Development (OT06 KN, p.62)  
**P. Salaun**: Cation mediated reduction of antimonate Sb(OH)₅⁻ at gold electrode (OT18 KN, p.74)  
**B. Erable**: Performances of bioelectrochemical technologies for energy passive wastewater treatment (OT30 KN, p.86)
## Scientific and Social Programme

**Tuesday 6th September**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 6 Room A</th>
<th>Session 6 Room B</th>
<th>Session 6 Room C</th>
</tr>
</thead>
<tbody>
<tr>
<td>02:20 PM</td>
<td><strong>B. Chefetz:</strong> Adsorptive fractionation of dissolved organic matter (DOM) by mineral surface (OT07, p.63)</td>
<td><strong>I. Mazerie:</strong> Design of Portable Sensor to Detect Pollutants in our Environment (OT19, p.75)</td>
<td><strong>S.Y. Ryu:</strong> Mixed-metal semiconductor anodes for electrochemical water splitting and reactive chlorine species generation: Implications for electrochemical wastewater treatment (OT31, p.87)</td>
</tr>
<tr>
<td>02:40 PM</td>
<td><strong>G. Fleury:</strong> ESI-FTMS study of the effect of mineral surface properties on the sorptive fractionation of soil fulvic acids (OT08, p.64)</td>
<td><strong>M. Plavsic:</strong> The characterization of polysaccharides in seawater accessed by electrochemical methods (OT20, p.76)</td>
<td><strong>S. Pandit:</strong> Bacterial Biofilm formation on carbon electrodes under influence of an electric field (OT32, p.88)</td>
</tr>
<tr>
<td>03:00 PM</td>
<td><strong>M. Avena:</strong> Ligand exchange reactions at the metal oxide-water interface. Equilibrium and dynamic conditions (OT09 KN, p.65)</td>
<td><strong>E. Company:</strong> Review and recent developments of AGNES: a stripping technique for the determination of free metal concentrations (OT21, p.77)</td>
<td><strong>H. Zhao:</strong> Transformation and products of organic micropollutants with the presence of humic substance in water during enzymatic catalysis (OT33, p.89)</td>
</tr>
<tr>
<td>03:20 PM</td>
<td>Fruit &amp; coffee break</td>
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<tr>
<td>03:40 PM</td>
<td><strong>L.K. Koopal:</strong> Surfactant Adsorption to Soil Components (OT10 KN, p.66)</td>
<td><strong>W. Davison:</strong> Maximizing mechanistic information from DGT-plant studies (OT22 KN, p.78)</td>
<td><strong>A.V. Delgado:</strong> New materials as electrodes for capacitive energy production (OT34 KN, p.90)</td>
</tr>
<tr>
<td>04:00 PM</td>
<td><strong>B. Embley:</strong> Modelling dust-control foams: Drainage into a fractal porous substrate (OT11, p.67)</td>
<td><strong>T. Nhu-Trang:</strong> Comparison between active and passive sampling POCIS for monitoring polar pesticides in Tra Vinh rivers (Mekong Delta) (OT23, p.79)</td>
<td><strong>Y.G. Mishael:</strong> Adsorption of Effluent Organic Matter by Polycation-Clay Composite Sorbents: Effect of Polycation Configuration on Pharmaceutical Binding (OT35, p.91)</td>
</tr>
<tr>
<td>04:20 PM</td>
<td><strong>H. Bertin:</strong> Foam Placement for Soil Remediation (OT12, p.68)</td>
<td><strong>T.H. Dao:</strong> Real-time X-ray Fluorescence in Probing Rhizosphere Processes Controlling Release and Losses of Phosphorus and Other Macronutrients (OT24, p.80)</td>
<td><strong>J. Zajac:</strong> Prediction of the effects of competitive adsorption in the dye removal from wastewater by layered double hydroxides: competition between anionic Orange-type dyes and inorganic divalent anions (OT36, p.92)</td>
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<tr>
<td>04:40 PM</td>
<td><strong>P. Behra:</strong> Comparison of sorption behaviour of different contaminants on natural aquifer sand (OT13, p.69)</td>
<td><strong>E. Anticó:</strong> Comparison of emerging techniques for Zn speciation measurements in a nutrient solution (OT25, p.81)</td>
<td><strong>T. Hofmann:</strong> Effect of ageing on biochar properties and intrinsic contaminant composition (OT37, p.93)</td>
</tr>
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</table>

05:00 PM  
**Poster session & networking**  
with drinks and snacks

08:30 PM  
**Social event: Gala Dinner**
<table>
<thead>
<tr>
<th>Time</th>
<th>Session 7 Room A</th>
<th>Session 7 Room B</th>
<th>Session 7 Room C</th>
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<tr>
<td>9:00 AM</td>
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<tr>
<td></td>
<td><strong>Laurent Charlet</strong> (OW01 P, p.94)</td>
<td>Advanced experimental techniques to probe environmental interfacial processes</td>
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<tr>
<td>9:50 AM</td>
<td><strong>Bert Hamelers</strong> (OW02 P, p.95)</td>
<td>The electrosorption process for energy generation</td>
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<tr>
<td>10:40 AM</td>
<td>Fruit &amp; coffee break</td>
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<tr>
<td>11:10 AM</td>
<td><strong>M. Gledhill</strong>: Investigating the impact of ocean acidification on the speciation of iron - a combined experimental and modeling approach (OW03 KN, p.96)</td>
<td><strong>M. Grzelczak</strong>: Self-assembled composite colloids and their application to SERS detection (OW08 KN, p.101)</td>
<td><strong>T.D. Waite</strong>: Nature, Extent and Implications of Redox Processes in Capacitive Deionization (CDI) Water Treatment (OW13 KN, p.106)</td>
</tr>
<tr>
<td>11:30 AM</td>
<td><strong>S. Chakraborty</strong>: Redox reactivity of Fe(II) sorbed on smectites: U(VI) reduction (OW04, p.97)</td>
<td><strong>H.A. Al-Abadleh</strong>: Organics on the Surface of Hematite Nanoparticles and the Environmental Fate of Arsenicals from ATR-FTIR, Surface Complexation Modeling and Flow Calorimetry Studies (OW09, p.102)</td>
<td><strong>P.M. Biesheuvel</strong>: The origin of pH fluctuations in capacitive deionization (OW14, p.107)</td>
</tr>
<tr>
<td>12:30 PM</td>
<td><strong>W. Tan</strong>: A vision for transformation of iron oxides with organic molecules in soil (OW07 KN, p.100)</td>
<td><strong>M. Sander</strong>: Viruses at solid-water interfaces: assessing major interactions driving adsorption and competitive effects on adsorption in the presence of dissolved organic matter as co-adsorbate (OW12, p.105)</td>
<td><strong>S. Ahualli</strong>: Use of soft electrodes for capacitive deionization (OW17, p.110)</td>
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<tr>
<td>01:00 PM</td>
<td>Closing Ceremony, Awards, Announcement of following IAP Meeting</td>
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<td>01:20 PM</td>
<td>LUNCH</td>
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<td>3:00 PM</td>
<td>Tutorial on Capacitive Deionization</td>
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Oral presentations
Interfaces Against Pollution: from nature to meet society’s challenges

S.L.S. Stipp and the NanoGeoScience Research Group

Nano-Science Center, Department of Chemistry, University of Copenhagen
E-mail contact: stipp@nano.ku.dk

The electronics revolution has provided us with analytical tools that make it possible to see directly at the molecular level. These instruments have been designed for characterising nanoscale technological materials but they can also be applied to the study of natural solid-fluid interfaces, to provide new information about the physical, chemical and biological processes that take place there. By learning how nature works, through understanding the fundamental processes, we can get new ideas for solving some of the challenges that society faces. There are many examples.

We have demonstrated that pore surface wettability is heterogeneous at the nanometre scale, using atomic force microscopy (AFM) with functionalised tips in chemical force mapping (CFM) mode. With quite a new technique, infrared spectroscopy combined with AFM, we can make chemical maps at nanometer resolution, where we can determine the composition of the material adsorbed on the surfaces of particles and pores. X-ray photoelectron spectroscopy (XPS) has proven that all mineral surfaces have associated organic compounds, even those in the pores of clean groundwater aquifers. This material offers anchor points for hydrophobic compounds and controls our ability to remove organic and inorganic contaminants. Results from CFM and XPS complement predictions from density functional theory (DFT) and molecular dynamics (MD), to show that sorption of organic molecules or ions can change surface tension dramatically. For example only 10% substitution of Mg²⁺ and SO₄²⁻ on a calcite surface can decrease the oil-water contact angle by 45 ° or more, depending on its initial value. This means that the composition of the pore fluids determines the effectiveness of removing organic compounds such as pesticides or chlorinated solvents. X-ray nanotomography (XNT), especially using ptychography, and focused ion beam scanning electron microscopy (FIB-SEM) yield 3D images with <40 nm voxel dimension, of the internal structure of porous materials, allowing prediction of porosity, permeability and other petrophysical parameters from soil, sediment and rocks. This allows us to determine where contaminants would be most likely to adhere and provides clues for how to remove them.

We work a lot with the private sector. An exciting aspect of our partnerships is that the new insight developed for solving one problem can be applied to many others because the work provides very fundamental understanding about nature. So our new knowledge about how to change pore surface properties to release more oil can be used for remediating contaminated soil. What we have learned about reacting CO₂ with basalt in Iceland to convert the gas to mineral form, is being applied to rock wool insulation. The effect of surfactants on mineral surfaces provides insight into how organisms control their environment, to biomineralise shells, bones and teeth. The ability to predict fluid behaviour in groundwater systems is equally applicable to other porous media, such as catalysts, filtration membranes and biomineralised material. Molecular scale insight about the processes that take place at fluid-solid interfaces can help us clean up current pollution and prevent future problems.
New Frontier of Bio-Nano Interactions

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Abstract:
It has been of interest to find guiding principles to help us understand how nanoscale objects interact with living organisms. Firstly, the nanoscale is unique in biology, and our capacity to engineer on that scale is transformative. The intrinsic machinery of biology is defined and operates on the nanoscale. Typical biomolecules and assemblies that are actively transported around organisms by specific motors and drivers are between 5-80nm. This means that nanoparticles are also actively transported around cells and biological barriers all unlike small molecules which passively partition into biological compartments (cells, organs, etc.). Secondly, the power of being able to communicate with, and use those endogenous mechanisms of biology is potentially transformative in practical terms. It is clear, and is often discussed how transformative could be the contribution of nanoscience to medicine, diagnostics, and new kinds of cell therapies.

However, with this enormous potential power to engage with the machinery of organisms there are also challenges. Firstly, the complexity of the interaction is remarkable, much more than for small cell and molecules, or large particles. Capturing this new capacity for benefit of human society will require dedication and commitment, indeed an exceptional generational effort, rather than peripheral research. To some degree, both the potential, and the challenge, of this field may have been underestimated, and only now are we beginning to face the need to invest in guiding principles and laws governing the whole arena. We also grow more confident in the potential, and our capacity to master it.

We discuss progress being made in understanding how interactions between nanoscale objects and living organisms occur, and their governing principles. [2, 3] We argue that the future lies in pressing forward to develop a truly microscopic (molecular scale) understanding between the nanoscale and living organisms.

References:
Manufactured nanoparticles in natural systems; some uses and questions

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E: j.lead@mailbox.sc.edu

Manufactured nanoparticles can be defined as materials which have at least one dimension between 1 and 100 nm and which are deliberately made for specific purposes, exploiting novel functionality. Nanoparticles have both potential uses and benefits and there has been great investment into them in a range of sectors. However, they also present potential environmental and human health concerns because of a lack of understanding of exposure, toxicity and novel functionality. This talk will discuss particular nanoparticle synthesis and analytical applications in remediation and in ecotoxicology. In particular, a facile, cheap and effective method for oil remediation and metal/oil remediation will be presented. The method works quantitatively under environmental conditions, is scalable to the production of >>kg/day quantities and stimulates natural oil remediation processes. Secondly, the development of new nanohybrid materials used to provide better understanding of mechanisms of action will be discussed. Finally, applications of single particle inductively coupled plasma mass spectroscopy (SP-ICP-MS) which will allow direct measurement of exposure and dose concentration at environmentally realistic concentrations will be presented.
Influence of Natural Organic Matter Model Molecules on the Aggregation of TiO₂ Nanoparticles

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Titanium dioxide (TiO₂) is one of the most used metal oxide nanoparticles due to its special properties. Nanomaterials are used in a wide variety of applications and their use has increased over the recent years, which leads to an increased amount of synthetic nanoparticles released into the environment. However, the fate and behavior of synthetic nanoparticles in the environment are not well-known. Nanoparticles generally have higher reactivity than larger particles of the same material, and this might influence the surface charging and aggregation behavior. Further, nanoparticles can interact with natural organic matter (NOM), such as humic and fulvic acids. Adsorption of NOM affects the surface speciation and net charge of the nanoparticles and is therefore of great importance for their colloidal stability.

The objective of the present study was to investigate the aggregation and adsorption behavior of synthetic TiO₂ nanoparticles in aqueous solution as a function of time in the presence of organic molecules. Synthesized and well-characterized TiO₂ (anatase) nanoparticles were used as test nanoparticles and selected phenolic carboxylic compounds were used as model substances to mimic the interactions of nanoparticles with NOM. In addition, a standardized fulvic acid was used in order to further mimic natural conditions. The aggregation and surface charging of the particles were studied by simultaneously monitoring the changes in particle size and zeta potential during the reactions using DLS. Also, a time study was made performed in order to observe potential changes in adsorption, surface charge and size over a time period of several months. Results show that both the type and position of functional groups on the organic molecules affect the aggregation behavior of the particles. Since the environment are is very dynamic, a study over a long period of time is of great importance for understanding the fate and potential risk of nanoparticles in the natural environment.
Natural Organic matter interfacial interactions with tannic acid-coated Silver nanoparticles (AgNPs): Implications on nanocontaminants mobility

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Nowadays, there is a strong increase in the production and use of nanoparticles in a numerous amount of products throughout the world. Due to their antimicrobial and antiviral properties silver nanoparticles have currently become one of the most commonly used NP type. For instance AgNPs found a wide application in medical healthcare, sunscreens, cosmetics, food industry and electronics. The rapid growth and the broad application have led to an increase of AgNPs discharge into the aquatic environment. The potential toxic impact of AgNPs on ecosystem and human health through possible chemical/physical transformations (i.e., sulfidation, dissolution, aggregation) has led to increasing concerns within the scientific community. This study should lead to a better understanding of the impact of NOM on AgNPs mobility dynamics and transport in aquatic ecosystems.

In this study the interfacial interactions of natural organic matter (NOM) with Tannic Acid (TA)-coated silver nanoparticles (AgNPs) as well as their aggregation kinetics were investigated by time-resolved dynamic light scattering (TR-DLS) and atomic force microscopy (AFM). A well-characterized NOM isolate, i.e., a river humic, was selected. TA-coated AgNPs were selected as a representative capped AgNPs. Aggregation of Ta-coated AgNPs was faster in Ca²⁺ solutions than in Na⁺ solutions. In river humic NOM solutions and in the presence of Na⁺, the aggregation rate of Ta-coated AgNPs did not significantly change. However, Ca²⁺ caused a dramatic increase in the aggregation of Ta-coated AgNPs in NOM solutions. AFM results confirmed the high affinity of humic NOM and TA for Ca²⁺ cations.

References
Sediments inhibit 17β-estradiol and 17α-ethinylestradiol adsorption by carbon nanotubes and graphene oxide: Effects of sediment particle size and organic matters

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With extensive application of carbonaceous nanomaterials (CNMs) in diverse realms, increasing amounts of CNMs will be released into aquatic environments. After released into natural waters, a major fraction of CNMs deposited into sediments because of their extremely hydrophobic properties. Both in water and in sediments, CNMs could interact with other pollutants, which would change the mobility, bioavailability, toxicity, and environmental risks of CNMs and pollutants. There have been considerable studies on the adsorption of pollutants by CNMs in aqueous solution, but far less research regarding the adsorption of contaminants by CNMs in sediments. In presence of natural sediments, CNMs would interact/heteroaggregate with sediments, which could alter the surface characteristics or blocking the adsorption sites of CNMs through coating and modification, and consequently impacts the pollutants adsorption by CNMs. Therefore, it is necessary to study the effects of sediments on the adsorption of pollutants by CNMs. Sediments contain a much wider range of particles with different particle sizes. The differences in the physical dimensions and compositions make different sediment particles showing distinct aggregation/interaction behaviors with CNMs. Significant advances in the effects of solution chemistry and natural organic matters (NOM) on the aggregation of CNMs and the adsorption of pollutants by CNMs have been made. However, at present, it is far from understood how and to what extent the particle sizes and organic matters (OM) of sediments influence their effects on pollutants adsorption by CNMs.

In this research, multi-walled carbon nanotubes (CNTs) and graphene oxide (GO) were selected as model CNMs, and 17βestradiol (E2) and 17α-ethinylestradiol (EE2), two typical endocrine disrupting chemicals, were chose as model pollutants. Sediment samples were collected from Nanjing of the Changjiang River (China). Sediments were separated into five particle size fractions: < 1 μm, 1-2 μm, 2-5 μm, 5-10 μm, and 10-63 μm, and the OM-free sediment samples were also prepared. The effects of sediment particle sizes and OM on the adsorption of E2 and EE2 by sediments alone and their mixtures with CNMs were investigated. The influencing mechanisms were explored using sedimentation experiments and transmission electron microscopy (TEM).

The results showed that the adsorption of E2/EE2 by sediments was extremely lower than by CNTs/GO, and the presence of sediments inhibited the E2/EE2 adsorption by CNTs/GO. Moreover, this inhibition effects were particle size-dependent: the smaller the particle size, the stronger the inhibition effects. This is ascribed to the interactions between CNTs/GO and different sediment particle fractions. The interaction of CNTs/GO with sediments increased with decreasing sediment particle sizes, which is governed by the BET surface area of sediments. On the other hand, the inhibition effect of sediments was also related to the shape or conformation of CNMs. Compared with CNTs, sediments showed greater inhibition effects on E2/EE2 adsorption by GO, because GO possesses an open-layered structure which has more accessible surface for interaction with sediments. FTIR spectra showed that CNTs/GO bind with sediments thought carboxylic groups on their surfaces. TEM images demonstrated that for the small particle size fractions of sediments (< 1 μm and 1-2μm), the CNTs were wrapped by the sediments and CNTs bridge the sediment particles. Whereas, for the large particle size fractions of sediments, CNTs were adsorbed on the surface of sediments particles besides homoaggregation. Different from the rolled tubular structure of CNTs, GO possesses a layer or sandwich-like structure. Therefore, GO was adsorbed by sediments through wrapping the outside of sediment particles. This led to fully attachment of GO on the surfaces of sediment particles, and consequently the adsorption of E2 and EE2 was inhibited significantly.

After removal of OM from the sediments, the presence of OM-free sediments still inhibited the adsorption of E2/EE2 by CNTs/GO. Moreover, the effect of OM-free sediment on E2/EE2 adsorption is also particle size-dependent, but the particle size-dependent effect became less significant. This is possibly attributed to the stronger interactions of CNMs with OM-free sediments than those with sediments, especially for larger particle sizes of sediments.

Acknowledgement - This research was funded by the National Natural Science Foundation of China (Grant No. 51379009).
Physical-chemical state and mechanisms of nanomaterial release from products during their life cycle: ageing effects at the products interfaces.

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The industrial scale production and wide variety of applications of manufactured nanomaterials (NMs) and their possible release into the natural aquatic environment have produced an increasing concern among the nanotechnology and environmental science community.

Even if a large piece of data is dedicated to address hazard of NMs few data exist on the exposure side, the second essential aspect of risk assessment. Environmental and consumer exposures will be based on many possible abiotic and biotic processes affecting stability (bio-degradation), fate, transport, and transformation of released nanomaterials. Moreover as function of the different stages of life cycle of product incorporating NMs, the structure, shape and properties of released NMs will vary. In many cases a change in the chemical form of NMs occurs during their life cycle due to ageing effects.

The study of nanomaterial releases from solid matrices (in which NMs are incorporated) is therefore an emerging field of research. Until now most efforts have focused on quantifying and identifying the released objects, providing valuable inputs to risk assessment models. However the mechanisms lying behind release are still largely unknown and rarely investigated.

The aim of this talk is to determine the mechanisms of NMs release during the ageing of products. Ageing generally leads to a modification of the product-environment interface controlling NMS release.

Various products case studies will be highlighted from self-cleaning cement, to wood coating, incorporating TiO₂-based and CeO₂-based NMs respectively.

We thoroughly analysed the aged solid matrices (from unaltered core to surface altered layer) using laser-ablation-ICP-MS and several X-ray based techniques: XRD (X-Ray Diffraction), µ-XRF (micro X-Ray Spectroscopy) and an unprecedented combination of nano and micro X-ray computed tomography to perform a complete altered matrix characterization including pore structure. Original results concerning the low-stability of the matrices while NOA are released in fresh water will be detailed with regards to the size and surface properties of nanomaterials.

Acknowledgment: This work is a contribution to the Labex Serenade (n° ANR-11-LABX-0064) funded by the “Investissements d’Avenir” French Government program of the French National Research Agency (ANR) through the A*MIDEX project (n° ANR-11-IDEX-0001-02). This work is also supported by the French X-ray CT platform called Nano-ID funded by the EQUIPEX project ANR-10-EQPX-39-01.
Silver nanoparticles in soil: aqueous extraction combined with single-particle ICP-MS for detection and characterization

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Abstract
Silver nanoparticles (AgNPs) have been incorporated more than other nanomaterials in a growing number of applications, and increasing amounts of these materials are contaminating the soil. The development of an efficient and powerful method to detect nanoparticles in soil is therefore required. The most recent methods use acid digestion of soil samples, which destroys the particles during extraction. We developed a method for extracting AgNP from soil without damaging the AgNP. Combining the extraction method with single-particle inductively coupled plasma mass spectrometry for detecting 60 and 100 nm AgNPs increased the power and speed of the method. The recovery rates for the combination were as high as 67.4% faster for clayey soil and 51.1% for sandy soil. The concentration recovery rates for 100 nm AgNPs (AgNP 100) was up to 70.1% in clayey soil and while for 60 nm AgNPs (AgNP 60) were up to 63.2% in sandy soils. AgNP particle-size recovery was 97% in clayey soil and 99% in sandy soil for AgNP 100 and 95% in clayey soil and 101% in sandy soil for AgNP 60. AgNP 100 was significantly less stable than AgNP 60 during the experiments. Fewer ions were released when soil samples were spiked with low AgNP 60 and 100 concentrations than with high concentrations. Validation of the method showed good performance for the trueness of AgNP particle size, at 106 and 95% for the sandy and clayey soils, respectively. The trueness of AgNP concentration was lower, at 32 and 46% for the sandy and clayey soils, respectively.
Single-particle element fingerprints for the detection of engineered cerium oxide nanoparticles in soils

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A major challenge in the field of environmental fate and ultimately risk assessment of engineered nanomaterials (ENMs) is the lack of analytical methods to detect and quantify ENMs in complex matrices (e.g. soils and sediments) against a high background of natural counterparts. In the case of engineered cerium oxide nanoparticles (CeO₂ ENPs), for example, detection is hindered by the presence of natural Ce-containing minerals of similar size and concentration ranges. A promising approach to identify CeO₂ ENPs against the natural background is to take advantage of the different element ratios of natural versus engineered Ce-containing nanoparticles (NPs). For example, the Ce to La ratio is expected to be relatively stable at about 2:1 in natural environments, while CeO₂ ENPs show a Ce:La ratio of about 4000:1. For a detection of CeO₂ ENPs in soils and sediments, we therefore need a method to assess the elemental ratios on an individual particle level.

We here present a new approach, using a prototype ICP-TOF-MS instrument [1], coupling a conventional ICP-MS with a time-of-flight (TOF) instrument, which enables the simultaneous measurement of multiple elements at high time resolution. The applicability of this method for the detection of CeO₂ ENPs in natural samples is demonstrated on natural soils spiked with different concentrations of CeO₂ ENPs. Our results show that we can differentiate between Ce- and La-containing natural particles and Ce-only containing ENPs using the ICP-TOF-MS in single-particle mode (Figure 1). A machine-learning based data processing method makes it possible to take full advantage of the unique multi-element fingerprints of both engineered and natural Ce-containing particles for the differentiation. This new method represents an important advancement for the detection of ENPs in complex matrices at environmentally relevant concentrations and can likely be applied to a wide range of other ENPs in the future.

References

Acknowledgements - The authors thank TOFWERK AG (Thun, Switzerland) for the use of the prototype ICP-TOFMS instrument. Funding is gratefully acknowledged from DetectNano (project number 8357508, FFG Austria), the Research Platform Nano-Norms-Nature (University of Vienna) and from COST action ES1205.
Screening and ranking of the redox- and acid-base reactivity during transformation and dissolution of manufactured nanomaterials in hydrous mediums: Valuable information for risk assessment?

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Manufactured nanomaterials (MNMs) are mono- and multiconstituent substances (nano-objects) in any shape with minimum external dimension below 100 nm. For regulatory implementation, the European Commission (EC) has recommended that a MNM should be any manufactured substance where 50% of the primary nano-objects by number are between 1 and 100 nm along their shortest external dimension, irrespective of whether they occur as individual nano-objects or in aggregates and agglomerates. In addition, the unique MNMs graphene, fullerene and single-walled carbon nanotubes are included by default.

Extensive research is currently conducted to improve our understanding on how MNM should be assessed in regards to their potential human and environmental effects and exposure along their lifecycle. One of the key aspects, is to which extent the (eco-)toxicological effects and fate is related to reactivities of the specific nanomaterials. In this work reactivity is considered to include electron donor/acceptor (redox) activity, acid-base reactivity, phase transformations, and dissolution of a MNM [1].

Despite the clear relevance, there are currently no commonly accepted standard methods or technical guidelines to determine these end-points in testing of MNM. To meet these challenges, two methods have been developed to study the short-term hydrochemical reactivities of MNM in different liquid mediums. A SensorDish® reader (SDR) system was applied for studying the variation of pH and O₂ over time during “open-air” incubation related to in vitro toxicological studies. In the SDR system, the atmospheric (5% CO₂ and 97%RH) and temperature (37°C) conditions are controlled ambiently in a cell-incubator. This method and protocol is currently under standardization in CEN/TC 352 WG2/PG1. The other method is a home-build Atmosphere-Temperature-pH (ATempH)-controlled Stirred Batch Reactor (SBR) with real-time monitoring of the added pH titrants and redox potential (Eₚ). The ATempH SBR is very suitable for studies that requires highly controlled test conditions. In both methods samples can be collected at any time-point for analysis of chemical and electron microscopy analyses of the residual test materials and potential reaction products. Whereas pH or acid-base titrant volume can be used directly to estimate the acid-base reactivity, the O₂ and Eₚ measurements can be used to assess the oxidative or electron donor potential of the MNM reactivity. This is an important end-point as electrons are the source for radical formation or direct oxidation, which are considered potentially detrimental in biological systems.

Results show that it is possible to identify pH and redox reactive MNM and their solubilities at fixed time-points in tests using these two systems. One of the most illustrative results was observed in a test of ZnO in different dispersion mediums for toxicological tests where ZnO as expected was highly dissolved after incubation in water, but transformed to Zn-phosphate in phosphate-buffered saline. The pH measurement suggested that the transformation into phosphate occurred within 2 hours after the dispersion was made. This illustrates the power of the methods to also assess reaction kinetics of the MNM. First comparison with in vitro and in vivo biological effects suggests a link between the obtained parameters and biological effects, which needs further investigation. The results will be further applied in reactin chemistry modelling. Results from studies of a.o. ZnO, mixed Fe-oxides, CeO₂, and carbon nanotubes will be presented and discussed.

References

Acknowledgement - The author gratefully acknowledge financial support from the EU FP7 project NANoREG (Grant 310584) and the Danish Centre for Nano-Safety funded by the Danish Work Environment Fund (Grant 49803) to conduct this work.
Interactions of nanoparticles with four fresh water algal strains

Renata Behra\textsuperscript{1}, Xiaomei Li\textsuperscript{1}, Kristin Schirmer\textsuperscript{1}

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Algae have been shown in many studies to be sensitive to various nanoparticles (NP), yet major questions still remain to be examined. For instance, it is generally not known whether assessed toxic effects depend on the cellular internalization of particles. Moreover, while other studies indicate that NP in the environment are prone to be transformed as a function of pH, ionic strength and chemicals which influence their fate, little attention has been given to the biological transformation of NP. Nevertheless, transformation processes similar to those that affect the fate of NP in aqueous solutions are expected to occur once particles interact with algal surfaces and components released by algae.

In order to examine the role of algae characteristics in influencing the fate of NP we have selected four strains of unicellular green algae displaying different surface characteristics. \textit{Euglena gracilis}, \textit{Haematococcus pluvialis}, and \textit{Chlamydomonas reinhardtii} wild type and a cell wall free mutant, were selected. Their interaction with fluorescent polystyrene nanoparticles (PSNP) of two sizes, 50 nm and 500 nm were investigated using confocal laser scanning microscopy. While no strain internalized PSNP, interactions of particles with algae were found to be unique for each strain and to depend on both the particle size and the characteristics of the algal cells, in particular their surface architecture and potential to secrete biomolecules.
Transport of waste-generated metallic colloids and nanoparticles in the Environment.

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During the last two decades, scientists showed the omnipresence of colloids and nanoparticles in the environment, emitted from a large panel of manufactured products and domestic wastes. The release into the environment of manufactured nanoparticles has considerably increased for the last ten years with the expansion of the nanotechnologies in the world, bringing emerging interests for nanomaterials emission, toxicity and fate since 2010s.

The challenge in assessing the predicted environmental concentration is that there are no standardized measuring methods for nanoparticles in the environment to this day. Furthermore there is no regulation and duty of declaration for nanoparticles and production volumes.

Lots of studies have highlighted the role of colloids in contaminant transport. Colloid facilitated transport of pollutants in the environment has been the subject of intense investigation over the last twenty years, and showed many contradictory results. The objective of our study was to quantify and understand the emission of nanoparticles from different types of wastes collected on the field and their transport through a porous media. We aimed at understanding their fate after dump disposal over time. Experimental columns tests were established with successive layers of solid waste and sand or kaolin to simulate potential release of these contaminants in waste disposal landfills. Percolates were collected over time to measure the size distribution and the chemical composition of the nano-size fractions. Nanoparticles Tracking Analysis (NTA) was newly developed for size and zeta potential determination on these heterogeneous samples (DLS was showed to be unsuitable), while SEM-EDX showed aggregation mechanism and interaction between metallic nanoparticles and natural organic matter. 3D fluorescence and carbon analysis allowed to track carbon percolation pattern in comparison with metal species (measured by ICP-AES) These results gave information about potential toxicity of wastes when they are leachated out in an open landfill site through soils, or when they are deposited in the bottom of the sea.

Regulations have to be made for the limitations of nanoparticles emission from domestic and industrial wastes.

We present here a new approach to characterize complex and heterogeneous colloids with NTA NS500 spectroscopy. Comparisons with DLS results are presented.
A Kinetic Environmental Fate Model for the Risk Assessment of Engineered Nanomaterials

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An integrated exposure model is proposed for the prediction of the environmental fate of nanomaterials (NMs) in various natural and man-made compartments. A semi-mechanistic approach is used, wherein the kinetic nature of the NM fate processes takes focus. Environmental matrix interactions depend on NM properties and relevant parameters, such as organic matter and ionic conditions, and are calculated on a temporal scale in each compartment. The obtained NM bioavailability is afterwards linked with existing hazard information. The goal of this approach is to apply the model for most currently-produced and possible future NMs, also aiming to find a compromise between mechanistical accuracy and operational simplicity.

The current model gives fate descriptors for soil, surface water, sediment and wastewater treatment plant (WWTP), and includes rates for key processes such as dissolution, sulfidation, heteroaggregation and sedimentation. A time-dependent approach is given to prioritize these key processes.

The WWTP is the main entry point for NMs emitted with domestic and industrial liquid waste. Partitioning of NMs in the WWTP, based on their affinity to sludge, determines the amounts that are transported to the surface water (in the effluent) and the soil (via sludge).

The physicochemistry of the surface waters, and the properties of the NM are among the factors that affect its bioavailable concentration in the water column and, after possible sedimentation, in the sediment within a certain time.

In the soil environment, focus is given on the top layer, where the NMs arrive also via the annual deposition of sludge. It is also in this layer where the most bioactivity and potential toxicity will occur. The time-dependent concentration in the pore water (liquid phase) and on the soil material (solid phase) is determined using a dual deposition model, allowing both NM release and irreversible attachment.

The time-dependency of chemical species concentrations is essential since it links exposure scenarios with hazards that change over time, which is critical in assessing NM bioavailability and eventual risks. This kinetic fate model is a key component in the web-based tool for the assessment and management of risks associated with NM-enabled consumer products, under the GUIDEnano Project (EU FP7). This work is also part of the NanoFASE Project (EU H2020).
Quantitative electron microscopy to probe nanoparticle dispersions and cellular uptake

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Nanoparticles are finding applications in strategically important fields, from healthcare to energy generation. When appropriately engineered they are the central and active component of a product, e.g. as agents for MRI contrast enhancement or the UV block in suncream. Nanoparticle size and surface coating are two of the property determining features, however these also enable uptake by cells leading to concerns regarding hazard to human health. Safety assessment of nanoparticles demands accurate and robust characterisation, and in this presentation we will present a systematic approach to the characterisation of nanoparticles and their cellular uptake using electron microscopy.

While it is common to use transmission or scanning electron microscopy (TEM or SEM) to measure primary particle sizes and confirm the elemental composition of nanoparticles, there is real potential for more far reaching studies to be performed. A key challenge for this work is representative sample preparation, with samples prepared by simply drop-casting suspensions not capturing any particle agglomeration due to drying processes that occur [1]. To overcome this problem we have prepared thin sections of nanoparticle suspensions for TEM by plunge-freezing a blotted grid into liquid ethane to ensure the aqueous phase vitrifies with no significant redistribution of suspended material. We have used this technique to quantify the dispersion of polymer coated quantum dots, silica and zinc oxide nanoparticles in water and biological cell culture media, identifying the true form in which these nanoparticles are taken up into cells in vitro and thereby providing mechanistic insight to the cellular response at these exposures [1,2,3].

Analysis can be extended into 3D, with the location, size and number of nanoparticle agglomerates taken up into cells quantified using serial block face SEM imaging [4,5]. Using this 3D information it is possible to correlate quantitative TEM imaging (which provides the location and number of nanoparticles per 2-D cell section) with that provided by other techniques (such as optical imaging), determining the nanoparticle dose taken up by a population of cells [4]. Combining analysis conducted on nanoparticle dispersions with cellular uptake, we have shown that electron microscopy is critical for the development of a data-driven modelling framework for the prediction of cellular uptake of engineered nanoparticles [5].

References

Organic matter dynamics in the Amazon river basin

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Freshwaters receive organic carbon from land and return back to the atmosphere a significant fraction of the carbon initially fixed by the terrestrial biosphere. A recent estimate based on the global land-flooded area suggests that CO₂ outgassing from inland waters and wetlands can offset the continental carbon sink. However, more than three-quarter of land-flooded areas all over the world are temporary wetlands, which role in the global carbon flows remains unclear. Here we show that in the central Amazon the magnitude of CO₂ outgassing from waters is spatially and temporally related to their connectivity with semi-aquatic vegetation. By combining our findings to published related data, we compute that this flux is large enough to support all CO₂ outgassing, which makes the central Amazon River and floodplains a close to neutral system with respect to atmospheric CO₂, rather than a large source as previously argued.

In aquatic systems, sorption of organic matter (OM) on environmental surfaces or its preference to remain dissolved is highly important for determining its potential transport and/or susceptibility to degradation resulting in the CO₂ fluxes discussed above. In the Amazon and other major rivers of the world, transported OM is either adsorbed to fine minerals or remains dissolved. Natural process leads to the remobilization of previously accumulated organic matter (OM) that is redistributed within soil profiles and exported towards rivers, hence their typical black coloration. The fate of autochthonous OM in Amazon floodplains and allochthonous OM from the river will be addressed by characterizing the nature of OM interactions with the sediment material. We investigate the fate of OM in the soil–water continuum in the Rio Negro basin through description of the composition of OM potentially mobile at different stages of podzol development and exploration of evidence for contributions from different soil horizons to the exportation of OM into waters. OM was water-extracted from seven key soil samples from a sequence representative of the transition between latosol and podzol on the low elevation plateaux of the Rio Negro basin, thus enabling following both vertical and lateral differentiations. The results demonstrate the existence of a decrease of size of the colloidal matter when passing from first order streams to higher order rivers (Figure 1).

Figure 1: Characterization of the colloidal organic matter from the Amazonian basin by asymmetrical flow field-flow fractionation and size exclusion chromatography.

Acknowledgement - This research is a contribution to the CARBAMA project, funded by the French National Agency for Research (grant number 08-BLAN-0221), the French INSU national programme EC2CO, and the National Council of Research and Development (CNPq), Brazil (Universal Program number 477655/2010-6).
Sorbed organic compound induces hydration of natural organic matter (NOM): A cooperative NOM swelling or a condensation in NOM environment?

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Interplay between interactions of organic compounds and water with natural organic matter (NOM) present in soils, sediments, aerosols and diverse geosorbents is of basic interest since its understanding may help to get insights into the “architecture” of this important natural material. It is also of great applied interest due to the fact that NOM controls sorption and environmental fate of multiple (natural and anthropogenic) organic compounds. Sorption interactions of organic compounds with NOM may need a cooperative involvement of several solvent (water) molecules [1-3]. The understanding of such a cooperative NOM hydration induced by presence of organic sorbates was based on considering that several “small” water molecules may be needed to hydrate/cover newly exposed internal NOM surfaces/sorption sites formed by incorporating relatively larger organic compounds into NOM [3,4]. Importantly, the earlier analysis was based on examining the effects of water activity on organic compound sorption by NOM [2-5].

There were no independent experimental proofs that (a) sorbing organic molecules may indeed bring water molecules into NOM, and (b) hydration of a local NOM microenvironment specific for a given organic sorbate occurs cooperatively with participation of several water molecules.

This presentation provides experimental evidences for organic sorbate-induced hydration of NOM. For that, a series of sorbents including three standard NOM-rich materials (i.e., a low rank coal, a NOM-rich peat and the humic acid sodium salt) and a clay-rich sorbent had been sequentially exposed to (1) water vapor over saturated aqueous salt solutions, and then (2) the vapor over the same saturated salt solution but containing dissolved phenol (no meaningful effect of dissolved phenol on water activity in a salt-saturated solution was found). In parallel, the control sorbent samples contacted continuously with the only water vapor over saturated aqueous salt solutions. The temporal changes in masses of sorbent samples were examined, and the mass increase caused by the sorbent exposure to the water/phenol vapor was compared to that obtained at the presence of the water vapor only. This difference was used to determine a sorbent mass increase due to the presence of phenol in a vapor-generating salt solution. The amounts of phenol actually sorbed were determined separately by applying the HPLC-based analysis of extracted samples. Experimental data showed that presence of phenol in vapor-generating salt solution resulted in a mass increase of sorbent samples, as compared with those contacting water vapor only. However, a phenol contribution to the mass increase was by about an order of magnitude less than a contribution of water molecules, sorption of which was enhanced by presence of phenol. This result provides the direct proof that sorption of a selected model compound induced a strong additional hydration of NOM sorbents. No similar effect was found for phenol/water vapor sorption on NOM-poor clay-rich sorbent. The ordinary effect of bulk condensation of phenol-water mixture was ruled out by examining the range of water activities in phenol-water binary mixtures. The observed organic sorbate-induced NOM hydration may be associated with different mechanisms, e.g., (a) a cooperative “dissolution” of both sorbates in NOM phase (~NOM swelling) or (b) forming phenol-water condensates at NOM surfaces and/or in confined NOM spaces (thus occurring at water activities essentially different as compared with those upon formation of normal bulk condensates). The probability of these mechanisms and their significance are discussed. In general, the data directly supported the concept of cooperative involvement of water molecules into organic compound-NOM interactions.

References
Leaching studies on marine shells using carbonated sea water

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Abstract
Leaching studies were carried out on marine shells using CO₂ acidified sea water for period of 30 days. Auger (hard) and transverse ark (soft) types of shells collected from Chennai coast were used. At the end of the period conducted in tank, the results of acidified and controlled sea water were analyzed and compared. Due to increase of acidity in carbonated sea water, calcium and bicarbonate content was increased averagely about 48% and 77% respectively. The weight decrease of shells was also monitored before and after leaching process. Percentage of weight decrease was occurred higher in acidified sea water. SEM images were also taken to find the corrosiveness in shells due to having higher acidity level in sea water. It clearly showed that there was substantial changes occurred in their morphological structure of shells due to leaching. While comparing results of soft and hard shells, leaching was maximum in soft shell than the hard shell.
The global biogeochemical cycle of selenium

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Selenium (Se) is an important micronutrient for humans and animals as it is present in the essential amino acid selenocysteine, which is incorporated in selenoproteins serving a wide range of biological functions. The structural similarity of selenocysteine to the sulfur analogue cysteine may lead to the unspecific incorporation of selenocysteine instead of cysteine in proteins. This is one of the reasons why selenium has a narrow range of safe intake concentrations, i.e. between 30 and 900 μg/day for humans [1].

Food crops are a main dietary source of selenium the contents of which are largely determined by the concentrations and forms of selenium in soils. However, selenium is often unevenly distributed in agricultural soils as well as in other environmental systems. In many regions of the world, the levels of selenium in soils and crops are low, which has resulted in insufficient dietary selenium intakes and associated environmental health issues. For example, in China, significant geomedical problems, including Kashin-Beck disease (an endemic osteoarthropathy) and Keshan disease (a cardiomyopathy) have been reported in low selenium districts. Selenium supplementation to affected populations has now reduced these health problems but it is still not clear which combination of factors controls selenium levels in soils on a broad scale. To understand why selenium is irregularly distributed in soils and why it is often present in low amounts and in forms that are unavailable for plants, it is important to better understand the mechanisms and pathways controlling distributions and bioavailability in soils.

Atmospheric deposition has been suggested to be an important source of selenium to soils and could therefore be a key factor explaining environmental selenium distributions [2]. This talk will give new insights into the atmospheric sources, sinks, and fluxes of selenium and will elucidate how different environmental pathways are linked. It will show how microorganisms (e.g., microalgae) produce volatile organic selenium compounds, which can potentially contribute to the atmospheric selenium pool [3,4]. Furthermore, it will show that marine productivity likely has another potential effect on selenium and possibly other trace elements in atmospheric deposition. The talk will also present how processes that control selenium distributions in soils can be used to establish large-scale geospatial predictions of selenium contents in soils using statistical models. The use of statistical models helps in advancing our understanding of the processes driving broad-scale distributions of selenium, and geospatial predictions will help prevent future health hazards related to unsafe levels of selenium in soils.

References
Intraparticulate metal speciation analysis: electrostatic and covalent contributions to binding of Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) by humic acid nanoparticles

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Soft and permeable nanoparticles are ubiquitous in environmental and biological systems where they play an important role in buffering concentrations of essential and toxic ions. A basic characteristic of an aqueous dispersion of such nanoparticles is that the reactive sites are spatially confined to the particle body which is at an electric potential different from that in the bulk medium. Accordingly it is necessary to define intrinsic descriptors that appropriately reflect the chemical speciation inside the particle's local environment. The speciation of divalent metal ions within the body of negatively charged soft nanoparticle complexants is elaborated for the example case of humic acid association with Cd(II), Pb(II) and Cu(II) in a dispersion with an excess background electrolyte. The electrostatic binding effects are defined on the basis of the binding of non-complexing Ca\(^{2+}\) ions and described by a two-state electrostatic model based on counterion condensation in the intraparticulate double layer and Donnan partitioning in the bulk of the particle.[1] Inner-sphere complexation is defined by an intrinsic binding constant (even free from the conventional outer-sphere binding constant, \(K_{os}\)) expressed in terms of local reactant concentrations as controlled by the pertinent electrostatic conditions. For all metals studied, at pH 6 and ionic strengths of 10 mM and 100 mM, the purely electrostatic association of their divalent ions with the oppositely charged nanoparticle is found to account for a substantial fraction of the total metal bound.

References
Isotopically exchangeable pool of Cr ($E_{w}^{\text{Cr}}$ value) in surface water: the colloidal contribution

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The labile pool of chromium can be efficiently assessed in environment through the use of isotopic dilution techniques ($E_{C}$ for soils [1] and $E_{w}^{\text{Cr}}$ for suspended matter into water [2]). The overall objective of this work was to evaluate the availability of Cr in different lotic and lentic systems, according to the range of suspended particle size (SPM) and, more specifically, to determine the role of colloids in the $E_{w}^{\text{Cr}}$ calculation. Surface water samples were collected in ponds and streams in June 2015 in Goiás State (Brazil) in the active nickel mine of Barro Alto. Two isotopic exchange (spike) experiments were performed. In the first experiment (# S1) the bulk samples were spiked and, after the equilibration time (48 hrs), filtered in cascade through 0.7 µm, 0.2 µm, 500 KDa and 1 KDa pore size membranes. In the second experiment (# S2), SPM (resp. colloids) were first separated according to their specific range of size (0.2-0.7 µm, 500 KDa-0.2 µm and 1-500 KDa) then independently spiked to assess the corresponding $E_{w}^{\text{Cr}}$ pools (Figure 1).

![Figure 1a and 1b: Design of spike experiments #S1 and #S2, respectively, and associated results.](image)

According to the results of experiment #S1, the $E_{w}^{\text{Cr}}$ pool in the ponds were higher than in the streams, with values up to 2200 µg/L in pond 1 and less than 163 µg/L in streams 1 and 2. In addition, the $E_{w}^{\text{Cr}}$ measured in the ponds were independent on the membrane cutoff, which traduces that labeled isotopes were equally equilibrated with natural ones, whatever the particle size. On the other hand, the streams displayed higher $E_{w}^{\text{Cr}}$ when using 1 KDa or 500 KDa than 0.2 µm or 0.7 µm cutoff membranes, which is contradictory to the previous findings of Lombi et al. [3], who convincingly demonstrated the existence of non-isotopically exchangeable metal in suspended sub-micrometer colloidal particles (SCPs) from soils suspension. The experiment #S2 highlighted additional differences between ponds and streams: whereas $E_{w}^{\text{Cr}}$ values were higher for large (0.2 – 0.7 µm) particles (7419 µg/L, 144 µg/L and 482 µg/L for pond 1, 2 and 3, resp.), $E_{w}^{\text{Cr}}$ values were higher for small (500 KDa-0.2 µm) particles or even colloids (1 – 500 KDa).

The SPM concentrations (>0.7 µm) in the ponds (219 mg/L) were 100 times higher than in the streams (2 mg/L), and XRD highlighted the presence of different Cr bearing phases in ponds (iron oxides, serpentine, phyllosilicates and spinels), and streams (magnesite and clinochlore). In addition, ponds were enriched in colloidal (<0.22 µm) and particulate (>0.22 µm) organic carbon (up to 5.48 mg/L and 10.11 mg/L, resp.) comparatively to the streams (up to 1.78 mg/L and 0.06 mg/L, resp.). This would suggest that $E_{w}^{\text{Cr}}$ is overestimated in the ponds by the presence of organic colloids, while in the streams contribution for organic colloids in the calculation of $E_{w}^{\text{Cr}}$ is negligible.

ISIDORE probe for trace metal speciation: from equilibrium to dynamic approach

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Up to now, different approaches have been proposed for in situ trace metal speciation, based on the deployment of in situ devices such as Donnan Membrane device (DMT) and then analysis by ICP-MS [1], or by means of preconcentration systems hyphenated with electrochemical detection such as gel integrated microelectrode (GIME) probe [2] or a direct in situ electrochemical stripping speciation method such as Absence Gradient Nernstian Equilibrium Stripping (AGNES) [3]. Although numerous in situ methods have been proposed, currently there is no reliable in situ probe for trace metal speciation at concentration levels present in natural systems. Regarding autonomy problems of in situ probes, electrochemical devices have the advantage of being easily available in smaller sizes and with the possibility to be operated with batteries.

This work presents the probe ISIDORE developed for in situ trace metal speciation [4]. This probe is based on the hyphenation between a DMT and a screen-printed electrode through a flow-cell (Figure 1), allowing a direct in situ detection and avoiding thus all problems inherent to sampling, transport and storage. The acceptor solution of the DMT was first optimized for electrochemical detection with a composition of 3 mmol L⁻¹ Ca(NO₃)₂ and 3 mmol L⁻¹ of sodium acetate buffer at pH 4.5. Under these conditions, the simultaneous determination of Zn, Pb and Cd is possible at low detection limits. The lower volume of the acceptor solution yielded a much faster equilibrium time, 6 h, as compared with the common 36 to 48 h deployment needed to reach equilibrium. The possibility of using the accumulation slope with ISIDORE is studied to further reduce the analysis time and obtain dynamic information on the nature of the metal complexes [5].

References


Acknowledgements - The authors acknowledge support of this research from the French national research agency ANR and the Portuguese national funding agency for science, research and technology (FCT-ANR/AAG-MAA/0065-2012 - SPECIES) and the Conseil Départemental des Pyrénées Atlantiques (CD64)
Addressing temperature effects on metal chemodynamics

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Temperature is a key parameter in metal chemodynamics experiments since it directly affects both the thermodynamics and kinetics of the chemical reactions and the transport of the species from the bulk to the surface of interest (electrode surface, biointerface, etc...)

Unfortunately there are very few metal chemodynamics or even metal speciation studies at different temperatures although they are certainly significant as demonstrated recently by Hassler et al [1] in the study of iron speciation in seawater at 4°C.

In this work we investigate the temperature effects on metal chemodynamics first for simple ligands (nitritotriacetic acid, iminodiacetic acid) and subsequently for colloidal dispersions of hard particles (carboxylated latex nanoparticles) and multi-responsive core-shell particles (PMMA-PNIPAM) in the temperature interval of 15 to 40°C.

These studies were carried out using Stripping Chronopotentiometry at Scanned deposition Potential (SSCP). The temporal and spatial scales of this study are respectively O(10−1 s) and O(10−5 m), characteristics of the thin mercury film rotating disk, used as working electrode. An evaluation of the metal calibration methodology for SSCP at different temperatures was conducted. It was found that although the variation of diffusion layer thickness can be correctly predicted, changes in standard reduction potential of the metals cannot, thus a calibration must be performed for each temperature studied [2].

For the small ligands investigated the lability degree and the association rate constant were evaluated in the temperature interval for a significantly non-labile system, cadmium binding by nitrilotriacetic acid, and a quasi-labile system, lead binding by iminodiacetic acid. Increasing the temperature induces a significant increase of lability of the small metal complex species resulting from two concomitant processes: (i) the expansion of the thickness of the diffusion layer, due to the increase of diffusion coefficients and decrease of solution viscosity with temperature (ii) the decrease of the reaction layer thickness arising from the augmentation of the association rate constant.

With the small complexes studied here the association rate constant follows a simple Eigen mechanism, while complexation of metal with colloidal ligands generally results from the coupling of the diffusive transport of free-metal ions M and the kinetics of ML complex formation/dissociation within the reactive component of the particle. The kinetic and the mass transport contributions in the association step generally depend on the electrostatic potential, the size, the hydrodynamic and complexation properties of the colloidal dispersions[3], thus the temperature effects observed differ from the observed for the small ligands.

The multi-responsive core-shell particles (PMMA-PNIPAM) change their structure as function of temperature, pH and ionic strength [4], thus the metal chemodynamics response to temperature is somewhat masked. Nonetheless we observe an increase in heterogeneity with increasing temperature which may lead to a loss of lability.

The temperature effects on metal chemodynamics are seldom studied but nonetheless very important in natural systems, hence we are currently interested in studying these effects in metal binding by natural organic matter and in the future in their mixtures with mineral particles.

References
Ion-binding properties of humic substance in deep sedimentary groundwater

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Humic substances (HSs) are ubiquitous in various environments and play an important role for the fate of pollutants. Deep underground environment is not an exception, although physicochemical and ion-binding properties of HSs there are largely unknown due to difficulties of their extraction. Based on limited studies on deep underground HSs, it has been recognized that they are distinctive from their counterparts in surface or shallow sub-surface environments. Thus, we have been studying humic and fulvic acids extracted from sedimentary groundwater at -250 m below ground surface at the Horonobe underground research laboratory, JAEA, including their chemical compositions, size distributions, spectroscopic properties, and ion bindings [1]. The aim of this talk is to demonstrate similarities and differences between the Horonobe HSs and surface HSs.

The extraction and purification of the Horonobe HSs is reported elsewhere together with their elemental compositions, carbon speciation by ¹³C NMR, size distributions, spectroscopic properties [1]. In summary, the Horonobe HSs consist of relatively small organic molecules rich in aliphatic carbons and reduced sulfur like thiol. Cluster analysis using the datasets of a wide range of the properties of the Horonobe and surface HSs from various origins suggests that they are statistically different.

Ion binding to the Horonobe HSs were studied by potentiometric titration for H⁺, Cu²⁺ and Cd²⁺, x-ray absorption spectroscopy (XAS) for Cu²⁺ and Cd²⁺, and time-resolved laser fluorescence spectroscopy (TRLFS) for Eu³⁺ [1, 2]. The binding amounts of these ions were fitted to the NICA-Donnan model. The densities of the acidic functional groups of the Horonobe HSs are comparable or slightly larger, compared with those of surface HSs, and their charge/pH curves are characterized by a steep increase of the negative charges around pH 4, followed by the rather gradual increase at pH > 6 (Figure 1), suggesting that the charge of the Horonobe HSs largely originates from de-protonation of chemically homogeneous low-affinity carboxylic-type functional groups. The binding of Cu²⁺ and Cd²⁺ to the Horonobe HSs are smaller than those to surface HSs over the entire pH and salt concentration investigated. In addition, the binding isotherms of these ions have slopes close to 1 in the log-log scale at acidic pH and those close to 0.5 at neutral to alkaline pH. This is somewhat odd, considering the high concentrations of the acidic functional groups of the former and can be explained by restricted formation of stable chelate rings with sparsely distributed functional groups on their aliphatic chains especially at low pH. XAS suggests that the contribution of sulfur-containing functional groups for the binding of Cu²⁺ to the Horonobe humic acid. In addition, the binding of Cd²⁺ to the Horonobe HSs are characterized by the presence of strong buffering, indicating the possibility of the formation of a solid phase. Unlike Cu²⁺ and Cd²⁺, the binding of Eu³⁺ to the Horonobe HSs are comparable to or even stronger than that to surface HSs and exhibits strong a salt effect. This indicates the importance of electrostatic interaction between the Horonobe HSs and Eu³⁺ and/or the presence of electrostatically induced changes of their structures or other properties. The latter might be the case as the NICA Donnan model failed to describe the Eu³⁺ binding to the Horonobe HSs when the binding data at different salt concentrations was simultaneously fitted.

References


Figure 1. Comparison of the charge/pH curve of Horonobe humic acid (HHA) and those of purified peat humic acid (PPHA) and purified Aldrich humic acid at 0.1 M salt concentration.
Dependency of Pb, Cd, and Zn binding on sources of dissolved organic matter

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This study evaluates the dependency of sources of dissolved organic matter (DOM) on metal binding (Pb, Cd, and Zn). Six different DOM samples (Suwannee River Humic acid (SRHA), Luther Marsh (LM), Amazon River (AM), Bannister Lake (BL), Burlington bay (BBL), and Desjardin Sewage (DS)), spanning gradient from allochthonous to autochthonous source, were collected by reverse osmosis for property characterizations (fluorescence, absorbance, acidity, and Cr-reducible sulfide (CRS)) and metal speciation experiments ([DOC] = 10 mg/L, I = 0.1 M KNO₃, pH = 8.0, titration range of [M] = 10⁻⁸.⁵ - 10⁻⁴.²⁵ M). The concentrations of Pb²⁺, Cd²⁺, and Zn²⁺ were measured by Absence of Gradient and Nernstian Equilibrium Stripping (AGNES). Overall, we found metal binding is DOM-source dependent. This dependency is most significant for Pb (e.g. 504-fold [Pb²⁺] variation), intermediate for Zn (e.g. 73-fold [Zn²⁺] variation), and least for Cd (e.g. ≤ 3-fold [Cd²⁺] variation). Moreover, there is a tendency that allochthonous DOM shows higher level of metal binding than autochthonous DOM, which can be explained relatively higher aromaticity in allochthonous DOM. To achieve reliable prediction of metal binding by Windermere Humic-Acid Model (WHAM) for source-specific DOM, the parameter of active DOM fraction (F) should be optimized accordingly (assuming 100 % fulvic acid for all DOMs). Defaulted F = 1.3 can only provide reliable prediction of Pb binding by very allochthonous and aromatic DOM similar to isolated humic acid materials (i.e. Specific absorbance coefficient at 254 nm; SUVA₂₅₄ ≥ 14 L m⁻¹ mg⁻¹ C⁻¹), but substantially overestimates the Pb binding by autochthonous DOM with less aromaticity (i.e. SUVA₂₅₄ ≤ 6 L m⁻¹ mg⁻¹ C⁻¹). Similar trend is found for Zn. However, the defaulted F = 1.3 can provides acceptable good prediction of Cd binding by all investigated DOM samples, irrespective of source variability. Optimal F values show strong linear correlations (R² = 0.82-0.96; p ≤ 0.01) with different optical proxies, indicating the potential of using simple measurement of optical properties to optimize F for predicting metal binding for site-specific DOM. F value for Pb and Cd linearly increases with increasing aromaticity (Specific absorbance coefficient at 346 nm; SCOA₃₄₆), whereas F value for Zn linearly decreases with increasing molecular weight (ratio of absorbance at 254 and at 365nm)and autochthonous features (fluorescence index). For better understanding of DOM source effects on metal binding, affinity spectrum was also calculated from a continuous-site Langmuir model (assuming 1:1 stoichiometric factor) using a fully optimized continuous method (FOCUS). Allochthonous DOM generally shows stronger affinity and higher capacity for Pb and Zn binding than autochthonous DOM. This tendency however, is not observed for Cd. To identify the possible chemical structures of organic ligands responsible for metal binding, the derived affinity spectrum is compared with the one predicted by Quantitative Structure-Property Relationship (QSPR), which is calibrated and validated by a set of affinity values for different molecular analogs from NIST database. Details of this comparison will be discussed.

![Figure 1](image-url)
Modelling of tri-valent metal binding to humic substances with the NICA-Donnan model

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The bio-availability and fate of metals in the environment is largely determined by their binding to particulate and dissolved organic matter. The humic fraction therein is considered the most important fraction with respect to metal binding. The binding of various metals to humic materials has been successfully modelled with the Humic-Ion-binding Models VI and VII and the NICA-Donnan (N-D) model [1, 2]. Fits of the N-D model for divalent metal binding to both fulvic- (FA) and humic acid (HA) are good with $R^2 > 0.90$ and RMSE generally below 0.20. The N-D fits for some of the trivalent metals, however, seem to be less accurate with $R^2$ of 0.60 or lower for Al, Cm and Am. A larger uncertainty in the data for these elements, [1] may explain the poorer fits to some extent. A more detailed look at the model fits than its evaluation by the overall performance in terms of $R^2$ and RMSE, might give more insight in possible shortcomings in parameterisation or model concept. For example, the fits by Mine et al. of Al binding to FA give a poor description of the pH dependence of Al binding on pH (see Figure 1, left panel), with an overestimation of Al binding at low pH (pH 3.6 - 4), whereas at higher pH (pH 5.5) Al binding is underestimated.

![Figure 1: Fits of Al binding to fulvic acid at various pH using generic proton binding constants from Milne et al. [1] (left) or Lenoir et al. [3] (right)](image)

Apparently the competition of Al with protons can not be described well by the combination of the derived binding constants for protons and Al. Superior fits to the data were found in case the binding parameters for Al were derived in combination with the proton binding parameters of Lenoir et al. [3], who derived optimum proton binding parameters for the same dataset as Milne et al. The logK values, especially those for the carboxylic groups derived by Lenoir et al. (logK₁ = 3.5) are clearly higher than those of Milne et al. (logK₁ = 2.3). Another possible reason for the poor fits could be the binding of hydrolysed species of Al by humic substances, which is not considered in the N-D model. The possible effect of including hydroxy-species in the N-D model will be evaluated using the combined PEST-ORCHESTRA tool [4] which enables the parameter optimisation of advanced models with the possibility to adapt them. The data set of Milne et al. and more recent data will be used to improve the modelling of trivalent metals with the N-D model.

References

Copper Binding to Soil Fulvic and Humic Acids: NICA-Donnan Modeling and Conditional Affinity Spectra

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Binding of Cu (II) to soil fulvic acid (JGFA), soil humic acids (JGHA, JLHA), and lignite-based humic acid (PAHA) was investigated through NICA-Donnan modeling and conditional affinity spectra (CAS). The objective of the present work is to extend the knowledge of copper binding by soil humic substances (HS) both with respect to enlarging the database of metal ion binding to HS and obtaining a good insight into Cu binding to the functional groups of FA and HA by using the NICA-Donnan model to unravel the intrinsic and conditional affinity spectra. Results showed that Cu binding to HS increased with increasing pH and decreasing ionic strength. The amount of Cu bound to the HAs was greater than the amount bound to JGFA. Milne’s generic parameters (Milne et al., 2003) did not provide satisfactory predictions for the present soil HS samples, while material-specific NICA-Donnan model parameters described and predicted Cu binding to the HS well. The obtained \( n_{Cu}/n_{HS} \) values indicated a significant bidentate structure of the Cu complexes with HS. By means of CAS underlying NICA isotherms, which was scarcely used, the nature of the binding at different solution conditions for a given sample and the differences in binding mode were illustrated. It was indicated that carboxylic group played an indispensable role in Cu binding to HS since the carboxylic CAS had stronger conditional affinity than the phenolic distribution due to its large degree of proton dissociation. The fact was especially true for JGFA and JLHA which contains much larger amount of carboxylic groups, and the occupation of phenolic sites by Cu was negligible. Comparable amounts of carboxylic and phenolic groups on PAHA and JGHA increased the occupation of phenolic type sites by Cu. The binding strength of PAHA-Cu and JGHA-Cu was stronger than that of JGFA-Cu and JLHA-Cu. The presence of phenolic groups increased the chance of forming more stable complexes, such as the salicylate-Cu or catechol-Cu type structures.

Figure 1: Occupation of JGHA and JLHA sites by Cu and the possible binding mode at given condition ([Cu\(^{2+}\)]_{total}=1×10^{-4} M, pH 5.0 and \( I=0.1 \) M). The black lines correspond to the global occupation by Cu. The orange areas represent the carboxylic type sites occupied by Cu; the yellow areas represent the phenolic type sites occupied by Cu.

References

Acknowledgement - The authors thank the Natural Science Foundation of China (Grant Nos. 41330852 and 41425006) and the National Key Basic Research Program of China (No. 2015CB150504) for the financially support.
Nanotechnology-Enabled Water Treatment: A Vision to Enable Decentralized Water Treatment and Reuse

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Through control over material size, morphology and chemical structure, nanotechnology offers novel materials that are nearly “all surface” and that can be more reactive per atom than bulk materials. Such engineered nanomaterials (ENMs) can offer superior catalytic, adsorptive, optical, electrical and/or antimicrobial properties that enable new technology platforms for next-generation water treatment. This presentation will address emerging opportunities for nanotechnology to meet a growing need for safer and more efficient decentralized water treatment and reuse. Examples of nano-enabled technologies that can enhance the removal of priority micro-pollutants include fouling-resistant membranes with embedded ENMs that allow for self-cleaning and repair; capacitive deionization with highly conductive and selective electrodes to remove multivalent ions; rapid magnetic separation using superparamagnetic nanoparticles; solar-thermal processes enabled by nanophotonics to desalinate with membrane distillation; disinfection and advanced oxidation using nanocatalysts; and nanostructured surfaces that discourage microbial adhesion and protect infrastructure against biofouling and corrosion. On the other hand, it is important to consider the unintended consequences of potential interactions with living beings. Because microorganisms form the basis of all known ecosystems and provide many critical environmental services, the implications of microbial-nanoparticle interactions will also be considered in the context of risks associated with accidental or incidental ENM releases. This analysis will focus on how water chemistry affects nanoparticle bioavailability, mobility, toxicity and reactivity, and how to steward safer and eco-responsible nanotechnology.
Water purification using oleate-modified magnetic nanoparticles

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Conventional treatment techniques to remove trace metallic elements from liquids are based on ion exchange, chemical precipitation/coprecipitation, reverse osmosis, concentration/evaporation, coagulation/flocculation, liquid-liquid extraction. These techniques offer satisfactorily extraction performances with limited amounts of effluent but revealed to be expensive especially when the use of solvents is required, long, with low recovery and sometimes unemployable when the volumes to be treated are large [1]. Recently, solid-phase extraction (SPE) principles have been investigated to get a simple, low cost, rapid, efficient and renewable extraction technique involving limited volumes of solvents. Decontamination methods using a magnetic assistance have also been actively developed by different scientific and R&D groups over the world in the last decade [2]. In this work, we investigated a synthesized composite magnetic adsorbent for the removal of nickel by solid-phase extraction from aqueous solution.

Magnetic nanoparticles of iron oxide (MNP) were synthesized, then the surface was recovered with oleate ions. The synthesized oleate-modified MNP were characterized (TEM, DLS, XRD, FT-IR, zeta potential, magnetometry), results showed that the 10 nm magnetite/maghemite nanoparticles (TEM photograph shown on Image 1) were structured with a double layer of oleate on the surface, as shown by FT-IR analyses, zeta potential measurements and the stability of the suspensions in aqueous medium. Then, the solution chemistry of oleate ions was studied in order to determine the CMC value (1.5-2.5 mmol/L) and the arrangement of ions above the CMC, whose structure and chemical properties (pKa) could be compared to the ones of the MNP. Results showed a structuration in vesicles around the pKa value (8.0) which was compared to the structure of oleate adsorbed on the MNP.

Nickel adsorption experiments were finally carried out from pH 5 to pH 9, and from 10^-6 to 2 10^-4 mol/L of nickel in 0.1 g/L suspensions of oleate-modified MNP. Retention of nickel was found to be highly dependent on pH, with a maximum adsorption (90%) beginning from pH = 7.5, close to the determined pKa value. The sorption isotherms were well fitted with the Langmuir model and the maximum nickel adsorption capacities were found to be 44 and 80 mg/g for pH = 6.8 and 7.2, respectively.

As a conclusion, adsorption on synthetic MNP was shown to efficiently remove nickel from aqueous solution. Adsorption isotherms showed a Langmuir-type behavior, this is in good accordance with others studies from the literature on surface-modified iron oxides. The maximum adsorption capacity for nickel depends on pH and is lower at acidic pH values due to surface protonation. This low adsorption at acidic pH values indicates that oleate-MNP can be regenerated by elution with a strong acid solution. The efficient removal of nickel combined with the magnetic properties of the NMP allow to propose the use of this system as a possible new effective water purification tool.

References
Removal of organic pollutants from wastewaters by magnetite/carbon nanocomposites

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Progress of various industries from the past decade led to a drastic increase in industrial effluent discharge, causing dramatically environmental pollution as well as serious life-threatening problems for environment. With regard to organic pollutants, dyes possess a high capacity to modify the environment due to their strong color and visual pollution and also cause changes in biological cycles mainly affecting photosynthesis processes. Phenols are most toxic to aquatic organisms even in low concentrations and have an adverse effect on the taste and odor of water [1]. Release of industrial effluent without proper and prior treatment into the environment is one of the major causes leading to a burden of health care issues in worldwide. For water purification, there is a need for technologies that have the ability to remove toxic contaminants from the environment to a safe level and to do so rapidly, efficiently and within a reasonable costs framework.

This work develops a methodology for selective removal of industrial dyes, and phenol derivatives from wastewaters using adsorption technology based on magnetic adsorbents. The magnetic nanoparticles embedded within a matrix of activated carbon (MNC) were synthetized by a simple and cost-effective combustion technique [2]. The influence of the magnetite/carbon nanoparticle ratio on the properties of the composites was also investigated. The samples were characterized by thermal analysis, X-Ray diffraction, FT-IR, scanning electron microscopy, specific surface area and particle size measurements, confirming that the as-prepared composites are made up of nanocrystalline Fe₃O₄ particles embedded within an amorphous matrix of activated carbon.

The magnetite/carbon nanocomposites were tested as adsorbents for removal of Chromazurol S (ChS), Basic Red 2 (BR2), and phenol derivatives: 3-aminophenol and p-nitrophenol from aqueous solutions. The effects of four independent variables: solution pH (2-11), initial concentration of pollutant (10-300 mg/L), adsorbent dose (1-4 g/L), contact time, and their interactions on the adsorption capacity of the nanocomposite was investigated in order to optimize the process.

The removal efficiency of pollutants depends on solution pH, and increases with increasing the carbon content, with initial concentration of the pollutants and the dose of MNC. Pseudo-second order kinetic model was fitted to the kinetic data, and adsorption isotherm analysis and thermodynamics was used to elucidate the adsorption mechanism.

The experimental data for pollutants adsorption on MNC showed a significant increase of the maximum adsorption capacity with the increase of the carbon content. Using an adsorbent mass of 1 g/L, an initial pollutant concentration of 100 mg/L, a magnetite/carbon ratio 1:3 (MNC2) and working at 25°C, the removal efficiency was 72.6% for ChS and 98.3% for BR2, respectively. In case of investigated phenol derivatives, the adsorption capacity of MNC2 increased in order: 3-aminophenol < p-nitrophenol.

The combination of high adsorption capacity, excellent separation capability and the short equilibrium time, indicates that the as-prepared magnetite/carbon nanocomposites are excellent adsorbent materials for organic pollutants.

References

Acknowledgement This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFSIDI, project number PN-II-RU-TE-2014-4-1319
Green synthesis of ultra-strong nanocomposite hydrogels for water treatment

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Due to its exceptionally high specific surface area and abundance of surface functional groups (including oxygen-containing hydroxyls, carboxyls and epoxides), graphene oxide (GO) has recently garnered attention as a high performance sorbent for dyes, heavy metal ions, oils and organic solvents from contaminated waters. However, recovery of GO after the decontamination process is difficult due to its highly stable nature in aqueous environments. Thus, self-assembly of GO sheets into porous 3D macrostructures such as hydrogels has been explored as a technique to exploit their high surface area while facilitating easy recovery from treated water. Still, forming mechanically robust hydrogels with acceptable adsorption capacities has been a significant challenge. We report a simple method for preparation of ultra-strong nanocomposite GO hydrogels at low pressure using vitamin C as a natural cross-linker. The structure and chemical compositions of the hydrogels are examined using microscopy and spectroscopy techniques. We demonstrate that hydrogels with high storage moduli can be used to effectively remove model dyes such as methylene blue, heavy metal ions and emerging contaminants such as diclofenac and sulfamethoxazole from aqueous solutions. We will describe the novel aspects of the hydrogel synthesis that give rise to its exceptional mechanical strength and adsorption capacity.
Adsorption of ibuprofen on a microporous carbon fabric, effect of ultrasound irradiation, competition with organic matter, and pore filling by a biofilm

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An efficient method to remove the micropollutants released at the exhaust of wastewater treatment plants is the adsorption on activated carbons. But this adsorption is limited by the presence of organic matter, the development of biofilms from bacteria, etc... Our objectives were firstly to study and model the influence of organic matter and biofilm on the adsorption kinetics of a model micropollutant (ibuprofen) on an activated carbon fabric and secondly to study the effect of ultrasound irradiation with the aim of accelerating the kinetics.

The activated carbon fabric (KIP1200, Dacarb, France) was characterized by SEM (Scanning Electron Microscopy), N₂ adsorption-desorption at 77 K, CO₂ adsorption at 273 K, and mercury porosimetry. The carbon fabric is exclusively microporous (S_{BET} : 1560 m²/g, V_{micro} : 0.54 cm³/g) and it is formed of woven strand made of three threads (about 300 µm diameter), composed of microporous fibre bundles (10 µm diameter). The fabric possesses two domains of macroporosity evidenced by mercury porosimetry: the first one in between the strands and the threads (1.94 cm³/g), and the second one within the thread in between the fibres (1.24 cm³/g).

The adsorption kinetics (or degradation) of ibuprofen at an initial concentration of 4 ppm (or 0.8 ppm) were studied at 13, 25 and 40°C. The adsorption isotherm at 25°C was also studied. The experiments were performed in 500 mL or 250 mL of buffered phosphate solution (pH 7.4 ; 0.04 mol L⁻¹) on an activated carbon fabric disk (12 mg). The time dependence of the ibuprofen concentration was analysed by high performance liquid chromatography. The kinetics were studied under stirring or ultrasound irradiation in a bath at 38 kHz, or by using a probe at 20 kHz. The effect of the fabric wetting on the kinetics was firstly studied. The impact of the dissolved organic matter at various concentration as well as the influence of a biofilm on the kinetics of adsorption of ibuprofen were studied. The biofilm was grown on the fabric through circulation of waste water (Total Organic Carbon=12-20 mg/L) weekly renewed. The adsorption kinetics on the fabric were simulated by a model of volume diffusion [1].

These simulations have allowed to obtain the values of the external mass transfer coefficient and the volume diffusion coefficient indicating that the adsorption kinetics are limited by the diffusion within the threads in the inter-fibre porosity.

The irradiation in an ultrasound tub (38 kHz) yields to a sharp acceleration of the adsorption kinetics (C/C₀=0.8 after 10h) with respect to the one obtained through magnetic stirring (C/C₀=0.2 after 10h). This is explained by a faster diffusion of the molecules under ultrasound irradiation and confirmed by the simulation using a diffusion model. The ultrasound irradiation at 20 kHz by using a probe coupled to adsorption (acoustic power of 60 W) in 500 mL yields to the ibuprofen degradation by the OH° radicals produced by the water sonolysis and thus can increase slightly the ibuprofen removal (C/C₀=0.8 after 6h). The competition with dissolved organic matter (humic acids, Total Organic Carbon = 4.4 ppm) decelerates the adsorption kinetics under ultrasound at 38 kHz (C/C₀=0.7 after 10h). The biofilm formed in the inter-fibre porosities (observed by confocal microscopy) has the effect to sharply reduce the adsorption speed (C/C₀=0.7 after 150h). The ultrasound irradiation in a tube (38 kHz) in presence of dissolved organic matter (TOC=4.4 mg/L) does not affect the adsorption kinetics of ibuprofen once the biofilm has been formed on the fabric.

References
Adsorptive removal of organic and inorganic pollutants from aqueous solution by surfactant modified alumina

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We investigated the removal of antibiotics, oxytetracycline (OTC) and ammonium ion (NH₄⁺) in aqueous media by using surfactant modified alumina (SMA). Surface modification of α-Al₂O₃ with anionic surfactant, sodium dodecyl sulfate (SDS) at high salt concentration induced a significant increase of the removal efficiency of both OTC and ammonium ion due to the presence of bilayer formation and/or admicelles [1]. The effective experimental conditions such as contact time, adsorbent dose, pH and initial adsorbate concentrations on the adsorption of OTC and NH₄⁺ onto SMA, of OTC and NH₄⁺ were systematically studied. The removal efficiencies of 91.4% and 95.2% were achieved at the optimum conditions for OTC and NH₄⁺, respectively.

The adsorption characteristics of OTC and NH₄⁺ onto SMA were similar in some points. At a fixed pH, the adsorption of OTC and NH₄⁺ onto SMA increased with decreasing NaCl concentration because desorption of SDS on α-Al₂O₃ surface was enhanced by increasing salt concentration (Figure 1). Experimental results of adsorption isotherms of OTC and NH₄⁺ onto SMA at different ionic strength can be represented well by two-step adsorption model. The change in surface charge and surface modifications of α-Al₂O₃ by adsorption of OTC and NH₄⁺ were evaluated by zeta potential measurements and Fourier transform infrared spectroscopy (FT-IR), respectively. Adsorption mechanisms of OTC and NH₄⁺ onto SMA were also discussed on the basis of adsorption isotherms, surface charge effect and surface modification.

Figure 1: Adsorption of OTC and NH₄⁺ onto SMA as a function of NaCl concentration (pH 4)

References

Acknowledgement: This research is funded by the Vietnam National University, Hanoi (VNU) under project number QG.16.12. T.D. Pham thank Nafosted for support to attend conference of IAP 2016.
Study of kinetics, thermodynamics and mechanism of defluoridation of drinking water using metal-loaded polymers

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Fluoride contamination in drinking water is a challenging environmental issue in recent years due to constant shrinking of fresh water resources. Increase in industrialization and various geochemical factors contributes to the increased fluoride concentration in ground water. Excessive ingestion of fluoride leads to bones and other health related diseases. World Health Organization (WHO) guideline has specified a maximum limit 1.5 mg L⁻¹ of fluoride for drinking water consumption. A number of low cost adsorbent materials such as activated carbon, kaolin, fly ash, etc., have been evaluated for defluoridation of drinking water. However, only a number of metals such as Al, Zr, La, etc., are known for their strong affinity towards fluoride. The present investigation reports fluoride adsorption using metal loaded polymeric materials, the later derived from natural sources. Thus, combination of a number of metals (in nano-phase) and number of functional polymeric materials such as chitosan, shellac and alginate were tested for their metal loading vis-à-vis fluoride removal capacity from drinking water.

The dependence of surface charge upon adsorption was studied from zeta-potential measurement and it was found that nonspecific adsorption of anions primarily involves colomic forces which is limited to pH dependent sites below the value of zero-point charge (pHpzc). The thermodynamics and kinetics of material-anion interaction was studied by variation of solution parameters. The adsorption process follows pseudo-second order kinetics (Table-1). The negative values of ∆G° at all temperature indicated the spontaneous nature of sorption process that occurred relatively at higher temperature. The positive values of both ∆H° and E_a confirms the endothermic nature of the sorption process.

<table>
<thead>
<tr>
<th>Pseudo-1st order</th>
<th>Pseudo-2nd order</th>
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<tr>
<td>Qₑ,cal R²</td>
<td>Qₑ,cal R²</td>
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<tr>
<td>0.392 0.992</td>
<td>0.370 0.997</td>
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Table 1: Kinetics of fluoride sorption by Zr-alginate hybrid

Presence of co-ions like NO₃⁻, Cl⁻, SO₄²⁻, except PO₄³⁻ and HCO₃⁻¹, had little effect upon fluoride sorption by hybrid material. Leaching of fluoride from hybrid material is negligible in acidic pH of the medium; whereas, alkaline pH (pH > 9) facilitates nearly 92% of leaching indicating reusable properties of materials. The detailed studies presented in the work establishes the novelty of the material properties for fluoride specific applications and thus supports further development towards commercial applications.

References

Acknowledgement - The authors thank University Grants Commission (UGC), New Delhi, for grant no. F-42 264/2013 (SR).
Building a Better Environment by Doing Things “Porely”

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Our program is concerned with the production and use of micro and nanoporous materials for a variety of environmentally friendly applications. This talk will be divided into the material science of building nanoporous oxide materials and to their practical applications. The first part of the talk will be devoted to the sol-gel chemistry of producing nanoparticulate oxides and thin-films composed of these oxides. In this first part of the talk, I will discuss the various physical chemical steps in the sol-gel process: sol-preparation, coating, gelation, drying and final firing of the materials. This is basically colloid chemistry and as well ceramic engineering. The second portion of the talk will touch on a variety of technologies that we are currently pursuing with particular attention to the use of these materials in ultracapacitors, cathode coatings in batteries, corrosion control, photocatalysis and photoelectrocatalysis, and capacitive water treatment. These are very different applications but all use our nanoporous oxide materials!
Water Chemistry Affects the Efficacy of Concentrated Suspensions of Iron Oxide Nanoparticles Used for Aquifer Reclamation

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Nanosized colloids of iron oxide enhance the subsurface microbial degradation of a wide range of organic contaminants and they are used as a technology to clean-up contaminated aquifers. These particles are synthesized with a coating of humic acids to increase their stability in aqueous suspension, a crucial property to ensure the subsurface mobility of concentrated slurries of this material. This study investigates particle properties, stability, and sedimentation in water as a function of chemistry and ionic composition. Goethite particles display high stability in different electrolyte solutions of NaCl and MgCl₂, consistent with a negative zeta potential of strong magnitude that implies an effective electrostatic stabilization. While goethite particles follow the predicted DLVO behavior in NaCl and show a high critical coagulation concentration, their aggregation is fast in the presence of calcium, even at very low ionic strengths (< 1 mM). This result is rationalized with the occurrence of bridging phenomena related to the interaction of calcium with adsorbed chains of humic acid, inducing fast flocculation and sedimentation of the suspensions. The dose of calcium, i.e., the concentration of calcium ions with respect to that of particles in the dispersion, is found to be the parameter governing these stabilization mechanisms. This result implies that more concentrated slurries may be more stable than dispersions of low particle concentration under certain conditions. Stability results correlate well with the extent of slurry transport within a column of saturated sand. These results suggest the possibility to design an effective remediation strategy for each specific site geochemical condition.

This work was partly funded by H2020 EU project ‘Reground’, G.A. n. 641768
Synthesis of Mg(OH)$_2$-coated nanoscale zero-valent iron (NZVI) for improved mobility and *in-situ* remediation in sand columns

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Nanoscale zero-valent iron (NZVI) has been extensively studied as an effective reactant for groundwater and soil remediation. With a high specific surface area, NZVI nanoparticles can be used for decontamination via reduction on the reactive surface. However, H$^+$ and dissolved O$_2$ in groundwater are also able to react with NZVI, i.e., corrode NZVI, forming an iron oxide layer on the surface, which greatly reduces the NZVI reactivity and even passivates entire particles. In addition, the magnetic NZVI nanoparticles aggregate together quickly to form larger clusters, making it difficult to deliver NZVI through soil to the contaminated area for remediation. In this study, a novel type of NZVI nanoparticles were synthesized with a soluble Mg(OH)$_2$ coating layer on the NZVI surface to form Mg(OH)$_2$-coated NZVI (NZVI@Mg(OH)$_2$). The core@shell structure can effectively improve the mobility of NZVI in porous media and protect the iron reactivity for an extended period of time.

After coating with the Mg(OH)$_2$ shell, the suspension stability of NZVI particles in aqueous solution increased remarkably. For the coating doses (Mg/Fe) of 0, 10, 20, 50 and 100 wt%, the half time (C/C$_0$ = 0.5) for particle sedimentation were 8.3, 34.9, 36.1, 53.0 and 128.6 min, respectively. The mobility of the NZVI particles was further determined by the filtration tests using sand columns (12-cm long and 1 cm in diameter filled with 0.3-0.4 mm silica sand). The results show that bare NZVI was unable to break through the sand column (Figure 1). Coating of Mg(OH)$_2$ onto the NZVI surface improved the mobility and transport of the particles significantly through the porous media. The breakthrough time of NZVI@Mg(OH)$_2$ decreased from 3.32 to 1.66 pore volume (PV) as the coating dose increased from 20 to 100 wt%. The breakthrough curve may be fitted by the following clean bed filtration mode, whose equation is , where C$_0$ and C are the concentration of NZVI in the inlet and outlet of the sand column, respectively, $\lambda_0$ is the filter coefficient, and L is the length of the sand column. As the Mg coating dose increased from 20 to 100 wt%, the $\lambda_0$ value decreased from 114.3 to 1.5 $\times$ 10$^{-3}$ cm$^{-1}$, implying a much extended penetration distance.

Moreover, the anti-corrosion property of Mg(OH)$_2$ coated NZVI particles also greatly improved, as the rate constant of NZVI corrosion by H$^+$ under an anaerobic condition decreased from 43.6 to 1.4 $\times$ 10$^{-3}$ mol-mol Fe$^0$ d$^{-1}$ with an increase in coating dose from 0 to 100 wt%. The results indicate that Mg(OH)$_2$ shell can effectively protect the reactivity of NZVI. The reactive NZVI surface can be well recovered for *in-situ* remediation with the dissolution of the Mg(OH)$_2$ coating layer by the flow of simulated groundwater. The *in-situ* remediation tests were conducted for removal of 1 mg/L Cr(VI) from the flowing water through the sand column containing 40 mg NZVI. Bare NZVI removed Cr(VI) completely within 246 PV and lost the reactivity after 563 PV (Figure 2). For the NZVI particles coated with 50 wt% Mg(OH)$_2$, the complete removal period was extended to 408 PV and the reactivity last for 1158 PV. The total reduction capacity of the NZVI for Cr(VI) increased from 46.5 to 79.3 mg/g (Cr/Fe) with the Mg(OH)$_2$ coating.

![Figure 1: Breakthrough curves of the NZVI@Mg(OH)$_2$ nanoparticles with coating doses from 10 to 100 wt%](image1)

![Figure 2: In-situ remediation of Cr(VI) by bare NZVI and NZVI@Mg(OH)$_2$](image2)
Preparation, Characterization and Applications of Electrospun Polyacrylonitrile Nanofibers

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The electrospun Polyacrylonitrile (PAN) and carbon nanotubes/PAN nanofibers were used as an adsorbed for the removal of iron ions from aqueous solution of iron chloride. The adsorbed iron ions were then converted into iron oxide nanoparticles and used for the photodegradation of dye in aqueous solution. The morphological study presented that the size of PAN nanofibers were below 400 nm and without beads while the size of nanoparticles were below 100 nm. The photodegradation study presented that the photodegradation of dye increased as increased the irradiation time. It was also found that the carbon nanotubes/PAN nanofibers degraded higher quantity of dye as compared to pure PAN nanofibers.

Figure: SEM image of Iron nanoparticles on PAN nanofibers
Strong and weak chelators conspire to control the bioavailability of trace metals to microbes

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In soils and in aquatic systems, microorganisms compete with each other to acquire essential trace metals. The principal weapons in this chemical warfare are metal chelating agents that are released by the organisms into the external medium.

In the first part of the talk, I shall discuss new data on the production of siderophores by N-fixing soil bacteria and their role in metal acquisition. New analytical techniques are providing an unprecedented view of the remarkable diversity of compounds that are produced, including strong and weak chelators, and highly soluble as well as amphiphilic compounds. Critical questions raised by these results include: why such variety of compounds? What is the role of the weak chelators? Are metals other than iron the object of this chemical warfare?

In the second part of the talk, I shall discuss the problem of trace metal acquisition by eukaryotic marine phytoplankton, focusing on iron and zinc, quantitatively the two most important algal micronutrients. Electrochemical data have demonstrated that, in surface seawater, these metals are complexed by strong chelators, the bulk of which are apparently produced by prokaryotes but only a few have been identified so far. There is no evidence that microalgae are able to take up directly strongly chelated trace metals. Instead these organisms rely on reductive mechanism and complexation by weak chelators to enhance the bioavailability of iron and zinc. How these processes are affected by pH is a key to the effect of ocean acidification on marine ecosystems.
Interfacial phenomena are also relevant for experiments run in the presence of NOM. Indeed, fulvic and humic acids have been shown to sorb onto the surfaces of phytoplankton cells at environmentally relevant pH values (4-7) and NOM concentrations (0-20 mg/L), and at various ionic strengths (0.002-0.1 M).[5-6] The association of NOM at cell surfaces is greater at pH 4 than at circumneutral pH, suggesting that the surface interaction of NOM involves either a hydrogen-bonding sorption mechanism, between electronegative functional groups present in the DOM and on the cell surface, or the formation of hydrophobic-bonds between the cell surface and the hydrophobic domain of the NOM.[5-7] The possible effects of this interaction on the adsorption, uptake and toxicity of metals will be explored.

References
Mercury species bioavailability to aquatic primary producers: from the cell to the community level

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Based on the extensive research over the last 30 years, bioavailability is accepted as a key concept allowing to quantitatively relate the changes in the trace metal concentrations and speciation with the intensity of the induced biological effects. However, in the case of mercury the interactions at ambient medium-biota interfaces are not fully understood, and the interconnection between the mercury speciation, bioaccumulation and biological effects is still to explore. Present work focusses on the bioavailability of inorganic mercury (IHg) and monomethylmercury (MeHg) to model phytoplankton species and periphyton communities, as representatives of the aquatic primary producers. The interactions of IHg and MeHg with green alga Chlamydomons reinhardtii during short-term exposure to IHg (20pM to 100nM) and MeHg (10 pM to 50nM) were studied at transcriptomic and physiological levels. The tested physiological endpoints included growth, oxidative stress and photosynthesis efficiency. RNAseq was used to examine mercury-induced perturbations of cellular metabolic pathways and to detect the earliest stages of the toxicological response. In complement to this lab-based work, the interactions of Hg species with periphyton communities were explored in the microcosm and in the field. The field experiments were performed in the Olt River (Romania) impacted by Hg-rich effluents from a chlor-alkali platform. Periphyton composition was examined by amplicon sequencing together with the accumulated IHg and MeHg. In parallel, the physico-chemical parameters of the ambient waters (pH, anion/cation and dissolved organic matter concentrations) were well characterized and IHg and MeHg concentrations measured in order to model dissolved IHg and MeHg speciation. Accumulated IHg and MeHg in both microalgae and periphyton were determined w/o cysteine washing to assess the total and intracellular Hg contents.

The main findings of this study can be summarized as follows. In the lab experimentation a linear increase of the intracellular IHg and MeHg contents in C. reinhardtii with the exposure concentration range was found. The number of dysregulated transcripts rised proportionally to the increase of the intracellular Hg contents of both IHg and MeHg. However for the comparable intracellular content, the number of the dysregulated transcripts was higher for MeHg than for IHg, suggesting stronger impact of MeHg on algae as compared to IHg. At transcriptome level, exposure to MeHg dysregulated the expression of genes involved in motility, energy metabolism, lipid metabolism, and transport and antioxidant enzymes in C. reinhardtii, while IHg induced similar alterations but only at highest exposure concentration of 100nM. At physiological level, sub-nM MeHg induced increase of the percentage of the cells experiencing oxidative stress, and affect the PSII, however no similar effects were detected for IHg in the studied concentration rage. At community level, a significant correlations were found between the IHg accumulation in periphyton and specific dissolved Hg species (Hg(OH)₂ and Hg(CO₃)₂ concentrations as well as the abundance of merA and hgcA genes. However no link of MeHg accumulation in periphyton with any studied chemical factor was found. Exposure to the pM levels of IHg resulted in a shift in periphyton community composition, favoring bacteria over algae. Bacterial communities were dominated by proteobacteria. The proportion of cyanobacteria and bacteroidetes was more important at higher Hg concentrations. An increase in the presence of the known Hg resistance gene (merA) that co-occurred with these community changes is in agreement with the Pollution Induced Community Tolerance concept. The results of the present study contribute to significant improvement of the understanding of Hg compounds interaction with green microalgae and periphyton, as well as to the development of sensitive genetic biomarkers and community bioindicators in support to efforts of mercury monitoring programs in aquatic systems.

Acknowledgement - The authors acknowledge the Swiss National Science Foundation projects IZERZ0-142228, 205321_138254 and 200020_157173 for the financial support.
Cyanobacteria is resistant to Hg and useful for its removal from aqueous medium

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Anthropogenic activities increased the input of Hg on its biogeochemical cycle. One possibility to reduce water pollution by metals in an economically viable way is utilizing the absorption/bioaccumulation capacity by aquatic organisms as a decontamination tool. The aim of this study was to evaluate Hg toxicity and potential of a cyanobacteria strain to remove Hg²⁺ from aqueous medium. Given the possibility of Hg methylation this study also aimed to evaluate the production of methylmercury by the cyanobacteria. Acute toxicity tests were performed using Nostoc sp. cultures grown in BG-11 medium. The salts HgCl₂ and CH₃HgCl were used respectively as Hg²⁺ and CH₃Hg⁺ sources. The cyanobacteria growth was daily monitored by absorbance during 96 hours. To evaluate Hg removal, final Hg concentrations (total Hg) in culture medium and in the biomass were determined using a Direct Mercury Analyzer (DMA, Milestone). To evaluate Hg²⁺ methylation cultures were exposed to concentration of 40 µgL⁻¹ for 30 days. The biomass was centrifuged, lyophilized and total Hg determined by DMA. The methyl specie was determined using gas chromatography-pyrolysis-atomic fluorescence spectrometry (GC-pyro-AFS) (MERX, Mark Brooks Rand Labs, USA). Hg biomass extraction was performed using a solution of KOH/methanol 25 % m/m [1]. The concentrations leading to 50% growth inhibition (EC₅₀) were 27.54 µg L⁻¹ and 30.87 µg L⁻¹ for Hg²⁺ and CH₃Hg⁺ respectively.

After 30 days of exposure to Hg²⁺, 18.95% from the total Hg remained in culture medium and Hg concentration in the biomass was 61.52 mg Kg⁻¹. Methylation was not detected in concentrations higher than the detection limit which represents 0.12% of the Hg present in the biomass. The Hg removal capacity results demonstrated that cyanobacteria cells are an efficient alternative to retain Hg even in low concentrations. It is important to note that methylmercury was not produced by the cyanobacteria. This would be a disadvantage as this is a toxic Hg specie and can be biaccumulated and biomagnified.

Reference:

Acknowledgement: The authors thank to Fundação de Amparo à Pesquisa de Minas Gerais-Fapemig, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-CAPES and Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq for financial support.
Kinetic and thermodynamic determinants of metal partitioning at biointerfaces: impacts of intracellular speciation dynamics

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A mechanistic understanding of the processes governing metal (M) toxicity to microorganisms (e.g. bacteria, algae) calls for an adequate formulation of metal partitioning at biointerfaces during cell exposure to M toxicants. This includes the account of metal transport dynamics from bulk solution to biomembrane and the kinetics of metal internalisation, both controlling the intracellular and biosurface metal fractions that potentially originate e.g. cell growth inhibition. Detailed formalisms1,2,3,4,5 are now available to evaluate such situations with a critical account of the electrostatic and structural features defining the biointerfaces, which offers physically-rich alternatives to the restrictive and often non-predictive equilibrium Biotic Ligand Model (BLM) framework. Despite these recent advances, there is still a need to rationalize how the dynamics of metal distribution at biointerfaces is impacted by the dynamic formation of intracellular metal complexes. In this presentation, we discuss a theoretical approach for examining how the kinetics and thermodynamics of biointerfacial metal distribution under non-complexing extracellular medium conditions is determined by the dynamics of intracellular metal speciation. The analysis makes use of concepts previously developed for chemodynamics of metal complexes in suspensions of (nano) particulate ligands.6,7 It leads to a rigorous formulation of ‘metal partitioning coefficient’ between intra- and extra- cellular compartments as a function of the relevant internalisation/excretion rate constants, M affinity to internalisation/excretion sites, and stability of intracellular metal complexes. The profound effects of intracellular M speciation dynamics on (i) the kinetics of M depletion from outer bulk solution, (ii) the limitation of M biouptake by diffusive transport, or (iii) the nature of the equilibrium M interfacial partitioning, are demonstrated on the basis of illustrative computational examples. Some of the fundaments of the theory are further supported by experimental data collected with electroanalytical probes on genetically-instrumented model bacteria.

References
Modelling Adsorption Processes at the Interfaces of Soil Particles - 15 Years Development

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Natural organic matter (NOM), metal (hydr)oxides and phyllosilicates are omnipresent soil particles, and they have high affinity for nutrients and pollutants. The interactions between these particles and various ions have been intensively studied. Advanced Surface Complexation Models (SCM) have been developed to describe the binary system of ion binding to individual type particles. Despite advances in the development of sophisticated models for individual type of particles, application of these models to natural environmental samples like soils and sediments is hampered by the complexity of the real systems.

About 15 years ago, the idea of Multiple-Surface Model was proposed to apply the surface complexation models for individual adsorptive surfaces to understand and predict ion speciation in natural samples. These studies focused mainly on the behaviour of cations. For simplicity, it was assumed that there is no effect of the particle interaction on the ion binding properties of the particles. Despite of these simplifications, rather promising results have been obtained for the metal ions Cu and Cd. For Ni, Zn and Pb, the model predictions are sometimes adequate, sometimes quite poor.

Following up research showed that the negligency of particle interactions in the Multiple-Surface Model leads to sometimes big deviations between the predicted and measured ion adsorption. For instance the interactions between the humics and oxides influence the binding of metal cations to both particles by site competition, electrostatic effects and formation of new ternary surface complexes. For anions, which bind strongly to metal (hydr)oxides and edges of clays and in general not to the humics, the effects of the particle interactions will reduce the affinity of the anions for the oxide and clay surface. This competitive effect can be of both chemical and electrostatic nature.

To be able to describe and predict the binding of cations and anions in environmental samples, a model framework that can deal with the adsorption of both inorganic ions and organic particles to minerals in a consistent manner is required. The concept of the Ligand and Charge Distribution (LCD) model was proposed about 10 years ago. The goal of the development of the LCD model is to have a model structure that can calculate the adsorption of both small ions and particles simultaneously in a consistent way and that can make use of the details already present in the advanced surface complexation models for oxides and humics. Promising results have been obtained in using the LCD model to describe adsorption of both cations and anions in soil samples (e.g. Figure 1 and 2).
Adsorptive fractionation of dissolved organic matter (DOM) by mineral surface

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Dissolved organic matter (DOM) represents small and labile, but highly important fraction of the soil organic matter (SOM) carbon pool due to its high reactivity. As one of the sources of subsoil organic carbon, DOM plays an important role in carbon cycling and distribution in the ecosystem. Thus, DOM composition and behavior affect various processes governing SOM accumulation and stabilization. One of the important aspects of DOM interactions with soils is its adsorptive fractionation.

In agricultural systems, DOM is ubiquitous and can be introduced to the soil from exogenous sources, such as wastewater and organic amendments. Thus, Comprehensive research on DOM compositional change as a results of interactions with reactive soil minerals is required. Though adsorptive fractionation of DOM by soil and minerals has been observed previously, quantitative evaluation of the change to the composition and physicochemical properties of DOM due to adsorptive fractionation by mineral are not yet investigated. In this research the adsorption and physico-chemical fractionation of DOM by clayey soil poor with organic matter was investigate studies. Two different sources of DOM were examined: DOM extracted from composted biosolids and DOM isolated from Suwannee River (SRNOM). Structural changes of DOM samples due to their interactions with mineral surfaces were studied by analyzing fractional composition of initial DOM solutions and that of supernatants obtained after DOM adsorption.

Sorption affinity of DOM samples to the studied soil was dependent on DOM source, which determines structure and chemical properties of DOM. SRNOM, which was characterized with higher content of aromatic and carboxylic groups demonstrated higher affinity to the studied soil. However, both types of DOM exhibited similar desorption behavior demonstrating significant sorption-desorption hysteresis. This suggests that DOM desorption was controlled by the dominant adsorbed DOM fraction, regardless of its source. Our hypothesis was further supported by the application of polymeric resins which demonstrated DOM adsorptive fractionation.

The resin separation of DOM to its compositional fractions showed that for both DOM sources the hydrophobic acid (HoA) fraction was preferentially adsorbed by soil surfaces and exhibited dependence on concentration. This fraction made up ~ 50% and 85% of total adsorbed carbon for compost DOM and SRNOM, respectively. As a result, the unbound DOM was enriched in more hydrophilic fractions. This suggests that DOM desorption was affected by HoA dominant adsorption to the soil fraction, and not by DOM source. The results of this study indicate that interactions of DOM with soil mineral surfaces result in an altered composition and may affect DOM reactivity in various physico-chemical processes in soils. Chemical and physical fractionation of DOM at the water-mineral interface must be considered in order to better predict carbon cycling as well as DOM bioavailability, mobility and reactivity towards pollutants, nutrients, and soil particles.
ESI-FTMS study of the effect of mineral surface properties on the sorptive fractionation of soil fulvic acids

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Introduction
Fulvic acids (FAs) are complex mixtures of thousands of organic molecules and are known to undergo a chemical fractionation during their sorption onto minerals of soils. Understanding of the sorptive fractionation of FAs onto mineral surfaces is thus a major issue in environmental sciences relating to the coupled cycles of natural organic matter and pollutants in surface geochemical systems. To address the effects of the surface properties of minerals (metal oxide versus clay) on the sorption-driven fractionation of FAs in soils, we investigated the sorption at acidic pH (3-5) of a FA (PPH, extracted from a vosgian beech forest) onto α-alumina and kaolinite with the aim of gaining molecular-scale insights into the chemical identity of preferentially sorbing (and not sorbing) FA compounds. Batch sorption experiments of PPH in alumina or kaolinite colloidal suspensions were carried at PPH-to-solid ratio of 5mgC/g, and the initial and supernatant solutions were analyzed by ESI(-)-FTMS. The results provided molecular-scale evidence of distinct mechanisms controlling the sorptive fractionation of FAs onto Al oxides and clay minerals, respectively.

Results and conclusion
A strong fractionation was observed upon sorption of PPH onto alumina, with a preferential retention of the polycyclic aromatic compounds (PACs) and of the highly oxygenated compounds among not-condensed aromatics (NCAs) and aliphatics (cf. Fig. 1a). Conversely, the major part of aliphatics (excluding the highly oxygenated ones) was left in solution. Study of -CO2 or -CH2 homologous series of compounds revealed a strong correlation between relative affinity of aliphatics and NCAs for the surface of alumina and acidity of these molecules. For the PACs and the poorly oxygenated NCAs, the relative degree of sorption of the molecules was shown to depend on molecular acidity (for compounds of higher O/C ratios) or on degree of hydrophobicity (for compounds of lower O/C ratios), which evidenced that sorption was mostly driven by reactions of ligand exchange on the surface or by hydrophobic interactions, respectively.

In contrast, the results obtained for PPH sorption onto kaolinite revealed a weak selectivity of this mineral surface. A large variety of compounds displayed a moderate affinity for the surface (cf. Fig. 1b), but only a few showed a very high affinity. Molecular acidity had only a slight effect on the degree of sorption of NCAs and aliphatics, and no relation was found between hydrophobicity of PACs or poorly oxygenated NCAs and their affinity for the surface. These results suggested that a main mechanism driving the sorption was hydrogen bonding between FA molecules and the low-affinity aluminol and silanol sites existing on the basal planes of kaolinite. Predominance of such a weak sorption mechanism accounted for the low retention observed for highly acidic FA molecules bearing oxygenated functionalities, whose sorption was prevented at pH 5 due to dissolved Al (released by kaolinite dissolution) competing successfully for their coordination.

Elucidating the distinct mechanisms involved in the sorptive fractionation of PPH onto a clay surface and a metallic oxide surface gave hints for understanding the contrasting sorption behaviours observed for divalent metals (e.g. Cd, Pb) and for Lanthanides, respectively, in sorption experiments and a beech soil system.

Figure 1: Van Krevelen diagrams showing the relative affinities of the FA compounds identified by ESI(-)-FTMS for the surfaces of alumina (a) and kaolinite (b) at pH 3.8 ± 0.1.
Ligand exchange reactions at the metal oxide-water interface. Equilibrium and dynamic conditions.

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Ligand exchange (or ligand substitution) reactions are key environmental reactions. They involve the exchange of one ligand for another in a metal complex, with no change in oxidation state at the metal center. These reactions are well-known by inorganic chemists that study the properties of metal complexes in solution, and by surface chemists that investigate the surface properties of metal oxides in aqueous media. A typical example of a ligand exchange reaction at the surface of a metal (hydr)oxide is the exchange of the herbicide glyphosate by phosphate at the surface of goethite (α-FeOOH). Another example is the desorption of glyphosate caused by the adsorption of humic acid (HA) on goethite.

Ligand exchange reactions result in the formation of inner-sphere complexes at the mineral surface, and many of these complexes can be experimentally detected by spectroscopies as infrared, Raman, synchrotron based spectroscopies, etc. With these techniques, the adsorption of the entering ligand and the desorption of the outgoing ligand can be simultaneously monitored as the reaction proceeds giving important kinetic information on the studied system. In addition, since the shape of the spectra is also evaluated as a function of time, the surface complexes and reaction intermediates can be sometimes identified, giving information on the reaction mechanism. Together with adsorption isotherms and surface complexation models, which explore the system under equilibrium conditions, a good understanding of environmentally relevant processes occurring at interfaces can be achieved.

This presentation focusses on adsorption-desorption processes that take place by ligand exchange at the goethite-water interface. Examples are given for the pairs of ligands glyphosate-HA and glyphosate-phosphate. Depending on the system, ATR-FTIR spectroscopy data, adsorption isotherms with single- and double-ligand systems and/or surface complexation models are used to obtain desorption rate constants, rate laws and to gain insights into the surface speciation and competition for surface sites.

![Figure 1: Example of ATR-FTIR signals as a function of time for adsorption of glyphosate (Gly) followed by adsorption of humic acid (HA). Spectra were recorded every 6 min of reaction.](image)

Acknowledgement - The author thanks CONICET, UNS, ANPCYT (Argentina) and CAS (China) for financial support of this research.
Surfactant Adsorption to Soil Components

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Soils are complex and widely varying mixtures of organic matter and inorganic materials; adsorption of surfactants to soils is therefore related to the soil composition. The most important types of soil particles are: humic substances, silica, metal oxides and layered aluminosilicates; their nature and charge density are important for surfactant binding.

The adsorption of surfactants on these soil components will be discussed, considering the specific (chemical) and electrostatic interactions, with hydrophobic attraction as an important component of the specific interactions and pH and ionic strength as parameters that govern the charge density of the particles.

Ionic surfactant adsorption is strong when the surfactant and particles are oppositely charged and at surfactant concentrations close to the CMC (critical micelle concentration) often bi-layer or admicelle type adsorption occurs.

In general, for a good understanding of the fate of surfactants in soil, the structure, hydrophobicity and charge of both the soil particles and the surfactant must be considered. As surfactant adsorption influences the colloidal stability of soil particles the soil structure and permeability are affected by the adsorption. Insight in surfactant adsorption to soil particles is therefore useful for good soil management and soil remediation.

References
Modelling dust-control foams: Drainage into a fractal porous substrate

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Coal mines must control dust in order to protect the environment and safeguard employee health. The conventional method involves spraying liquids, but foaming products generally perform better [1]. Prolonged release time of liquid and the stability of the foam may be factors in this improved performance. Both of these factors depend on foam drainage.

Foam drainage—that is, the flow of liquid between contiguous bubbles under the action of gravity and capillary suction—is generally well understood [2,3]. The process has been studied in conjunction with porous substrates in the past [4], but these studies, focused on organic pores such as those found in skin and hair, have not considered a fractal substrate (rather, all pores have been treated as uniform in size). In this work, the well known foam drainage equation is implemented atop (and bounded by) a fractal porous substrate, effectively modelling foam drainage into soil, stone, or coal dust [5–7].

In the model, bubble walls are treated as rigid (thus determining the foam drainage equation) [3], and the fractal substrate, considered to be semi-infinitely deep relative to the foam layer, is characterized both by a fractal dimension \(1 < D_f < 2\) and a tortuosity \(1 < \tau < 2\). Average pore size is varied in a range common to many inorganic substrates.

It is found that increased fractal character and decreased tortuosity result in more rapid liquid imbibition into the substrate and thus a faster “drying” of the foam and depletion of “wetting” or dust-controlling resources. Detailed transient results are presented for the fractal dimensions and tortuosity parameters of known inorganic substrates (coal dust, sandstone, and soil). Results are compared to the drainage of a foam into a non-fractal porous substrate, which is in fact a special case \((D_f = \tau = 1)\) of the generalized model presented here.

References

Foam Placement for Soil Remediation

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Foam can be generated in porous media by co-injecting gas and a surfactant solution, gas bubbles are generated mainly by snap-off phenomena and occupy a large part of the pore volume. The liquid films that separate the gas bubbles, called lamellae, and the gas trapped in the small pores where capillary pressure is high, generate a resistance to flow that decreases drastically fluid mobilities.

We present an experimental study starting with foam generation and propagation in sandpacks porous media of different permeabilities (from 0.25 to 80 Darcy). Gas and surfactant solution are injected at a constant flow rate and quality (85% of gas and 15% of liquid) while pressure drop and water saturation are measured continuously during the foam flow. Results show that foam is quickly generated and induces a piston-like displacement of liquid initially present in the porous media. The resistance factor (RF), which is the ratio between pressure drop measured when foam is flowing and pressure drop when only water is flowing, depends in a non obvious way [1] on permeability and capillary pressure (Figure 1). This dependence can be explained through the lamellae disjoining pressure trends in the different porous media.

Experiments performed on a 2D laboratory pilot (1 x 0.5 x 0.02 m³) made of two sand layers of different properties (8 and 80 Darcy) clearly highlight that foam is generated in the high permeability layer (Figure 2) and will divert flow towards the low permeability region. This behaviour is of great interest for the remediation of heterogeneous polluted soils because it can block the flow in the high permeability zones which are easily swept and divert it towards the non swept ones.

References

Acknowledgement - The authors thank INNOVASOL, an industrial fundation supported by EDF, ENGIE, SNCF, TOTAL and Conseil régional d’Aquitaine for their financial support of this study.
Comparison of sorption behaviour of different contaminants on natural aquifer sand

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In order to better understand the sorption mechanisms of different contaminants on natural aquifer material and compare their fate in the environment, both batch and column experiments were performed by studying the role of physical-chemical and/or hydrodynamic parameters such as pH, ionic strength, electrolyte composition, ligand concentration and flow rate. The natural aquifer sand, sample extracted from detritic sediments of the Vosges mountains (France), was mainly composed of amorphous silica and quartz (99 %), alumina-silicates such as feldspars (1 %) and clays (0.1 %) plus some traces of pyrite and of (hydr)oxides of Fe and Mn. Its specific surface area is rather low 0.16 m²/g and its point of zero charge around 6, what shows the effect of the presence of Fe (hydr)oxide coating at the surface of main minerals. The main compounds studied were: Ag(I), As(III) and As(V), Cd, Cu(II), Hg(II), Pb, phosphate, organotin (TBT, tributyltin), and humic acid (HA). Concentration range was from nM to mM depending on the chemical studied. For some of them, competition experiments were performed. Dissolution of Al, Fe, Si… from sand minerals was checked by ICP-MS, ICP-OES or IC analyses. Analytic speciation was performed for some compounds such as As, Ag, Fe, and organotin. Some surface analyses by XPS were also performed for a better knowledge of surface speciation.

Sorption of Cd, Cu, Pb and TBT did not depend on time contrary to the other compounds. Sorption kinetics of Ag was rather low, equilibrium being reached after 4 days. Hg and As sorption depends also strongly on time, flow rate changing their fate. Redox state of Cd, Cu, Hg, Pb, phosphate and TBT was stable, while Ag(I) and As(V) can be reduced depending on experimental conditions.

Sorption depends on the affinity of compounds to specific minerals. The strongest sites are: (hydr)oxides and clays for Ag, Cu, Hg and Pb; (hydr)oxides for As and Cd; mainly silica for TBT. Due to mineral dissolution, Fe, Al and sulphate are present at rather high concentrations. Fe content is much higher than the concentration which would be expected in the case of equilibrium with Fe(III) (hydr)oxides at a given pH. Traces of pyrite appeared as the main source of Fe and sulphate, controlling the redox, explaining Ag(I) or As(V) reduction. Moreover pyrite and Fe(II) (hydr)oxides can affect speciation of some of these compounds during experiments.

Comparing global affinity of compounds, it comes the following sequence for comparable experimental conditions: Ag > Hg > Pb > Cu > TBT > Cd > As(V) ≈ phosphate. Strong HA retardation occurred for pH < pzc, while HA behaved as a tracer at pH > pzc. On the other hand it was shown that clays can play the role of colloidal scavenger of trace elements during their peptisation by changing ionic strength due to input of water with a lowest salinity.

The main conclusion of such an overview is that all the minerals, even those present at low surface concentration, can control the transport of trace compounds meaning that it is necessary to get the best knowledge of their speciation and sorption mechanisms at atomic scale for reactive transport modelling at larger scale. It would be important for long term subsurface waste disposals.

Acknowledgement - This abstract summarized the different works of M. Hernandez Cortazar (Strasbourg) and D. Charrière (Toulouse), V. Trommetter, A. Hagège, F. Lagarde and M. Leroy (Strasbourg), Annalisa Bianchi, C. Grimaldi, M. Petrangel, Papini and M. Beccari (Roma), V. Wernert (Strasbourg and Karlsruhe) and F. Frimmel (Karsruhe), E. Lecarme-Théobald, J. Lambert and J.-J. Ehrhardt (Nancy), M. Bueno, A. and M. Astruc, I. Le Hécho, A. Chappaz and M. Potin-Gautier (Pau), J. Douch, M. Hamdani and R.A. Akbour (Agadir). All of them are acknowledge for their contribution.
Multiscale modelling for decontamination of aqueous solution using porous oxides.

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Decontamination and depollution commonly very often use charged porous media. The most well known example is probably ion exchange membranes used e.g. for electrodialysis or diffusion dialysis. Further materials are porous oxides. They are less widespread, but they have numerous specific applications, mainly because of the durability. In the context of nuclear energy, they are especially useful because they can relatively well resist to radiolysis. We describe a multiscale approach in order to describe ion separation and specific effects in two examples of porous oxides: silica glasses1,3 and nonatitanates2.

Figure 1: Multiscale description of silica glasses

The method we proposed in based on a molecular model. Atomistic simulations allow the evaluation of the interaction between the ions and the surface of the material. The calculation of the adsorption constant expresses the nature of the surface (hydrophilic, hydrophobic, etc.) and the role of the solvant. Then in a second stage macroscopic modelling can leads to the macroscopic parameters used in chemical engineering, in agreement with global experiments. Considering the large time and space scales in such systems, only such multiscale procedures can reproduce the complex nature of these materials.

In the case of silica glasses, we especially investigated the so-called Stern layer in order to understand ion adsorption. It is shown that Contact Ion Pairs (CIP) are formed for any alkali ions. They strongly depend on the nature of the interface and on the chemical conditions. A detailed analysis in terms of Density Functional Theory is proposed in order to improve the validity of the classical models based on the Poisson-Boltzmann equation. We also studied the decontamination of strontium performed thanks to sodium nonatitanates. In that case, contrary to silica glasses, ion exchange is driven by short range adsorption forces instead of long-ranged electrostatic interactions. Several adsorption sites appear as a function of the pH.

Such a procedure can also be applied to geological media (clays). Even if the prediction of decontamination appears to possible, it is worth noting that the method can only be performed if the molecular structure of the solid part of the material is known.

References
The molecular origin of zeta-potentials as revealed by non-equilibrium molecular dynamics simulations of a realistic mineral-aqueous solution interface

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Non-equilibrium molecular dynamics simulations of electroosmotic flow between parallel slabs of the hydroxylated (110) rutile (TiO₂) surface were utilized to estimate aqueous solution streaming mobilities, which were converted to zeta-potentials via the commonly used Helmholtz-Smoluchowski equation. A range of rutile surface charge densities (0.1 to -0.4 C/m²), corresponding to pH values between about 2.8 and 9.4 in RbCl, NaCl, and SrCl₂ aqueous solutions, were modeled and compared to experimental zeta-potential data for TiO₂ particle suspensions. Simulated zeta-potentials are in accord with experimental values including changing from positive to negative values with increasing pH at all RbCl and low NaCl and SrCl₂ concentrations, and remaining positive at higher NaCl and SrCl₂ concentrations. We show that the zeta-potential response primarily results from the gradual increase in mobilities of water and ions within about 15 Å of the surface, even in dilute solutions. The magnitudes of these electroosmotic mobilities are specific to a given water-solid interface and result from viscous drag between adjacent water layers and interactions with interfacial ions. This contrasts fundamentally with continuum descriptions of such interfaces, which postulate that the zeta-potential is the potential at a ‘slipping plane’ between immobile electrolyte at the surface and the bulk electrolyte.

Figure 1: Schematic picture of the molecular origin of electro-osmotic velocity

Figure 2: Zeta-potentials from NEMD simulations. Reference experimental data for rutile in NaCl are given as black symbols.

References
Inner surface potential measurements and interpretation of equilibrium at electrical interfacial layer

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The accumulation and binding of ions at the solid/aqueous electrolyte solution interface is the basis of most surface chemical processes [1]. The electrical charging at a metal oxide surface in aqueous environment, assuming formation of charged surface groups and their partial association with counterions, has been commonly described by the Surface Complexation Model (SCM). According to the SCM the state of charged surface sites is affected by the inner surface potential so that numerous attempts were made to measure this quantity. Experimentally, the construction of single crystal metal oxide and silver halide electrodes has enabled the measurement of open circuit potential and evaluation of the inner surface potential of defined crystal planes [2]. Such experimentally obtained data can be interpreted by the SCM and are in accordance with predictions of the Multi-site Complexation Model. The electrokinetic potential, i.e. potential at the electrokinetic slip plane, of same crystal plane can be obtained via streaming potential (or streaming current) measurements. The comparison and analysis of this two measured potentials leads to interesting and surprising findings. Electrostatic potentials are directly related to binding and distribution of charged ionic species at the interface and this mutual dependency is crucial for understanding the processes at the solid/aqueous electrolyte solution interfaces [3].

For some metal oxide crystal planes the measured surface potential and electrokinetic potential give unexpected results. While the measured inner surface potential is zero, the electrokinetic measurements for the same particular crystal plane provide a higher (absolute) values of the zeta potential. This finding could be explained by considering the pH dependent charging of the interfacial water layer via protonation or deprotonation, resulting in the presence of physically adsorbed hydronium or hydroxide ions. While the pH of the electrolyte solution affects the electrokinetic behavior but not the surface potential, the specific adsorption of strongly bound ions to oxide surfaces affect both the inner surface and zeta-potentials.

References
Dynamics of water soluble polyelectrolytes at the occasion of adsorption on the surface of colloidal particles probed by flocculation properties

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Dynamic behaviours of polyelectrolytes and neutral polymer on the surface of colloidal particles just after the incubation with bare colloidal particles were analysed using the flocculation properties of mono-dispersed PSL particles. Here, we define flocculation properties as physical properties which are intrinsically important to the analysis of flocculation. Effects of ionic strength, charge density of polymer chain and the presence of shear on the rate of flocculation, electrokinetics and the thickness of adsorbed polymer layer were analysed focusing the distinguishable nature of bridging formation and charge neutralization. Application of excess dosage of polymer in the normalized mixing result in the bridging flocculation yielding a clear cut of transient behaviour of polymer conformation from bulk solution to more or less flattened surface conformation. In the regime near optimum dosage of high charge density polymer, charge neutralization is dominant and advantageous for the continuous progress of flocculation by heterogeneous double layer interaction. Bridging flocculation takes places in the case of low charge density polymer or neutral polymer. Fluid mixing is considered to have essential role in the formation of bridges. In the case of neutral polymer, shielding of surface charge was found to be incomplete in terms of electrokinetics measurement. Crossover from bridging to charge neutralization as a function of elapsed time after the onset of mixing is confirmed for the case of high charge density polymer.

References
Cation mediated reduction of antimonate $\text{Sb(OH)}_6^{\text{-}}$ at gold electrode.

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Antimonate is notoriously difficult to reduce electrochemically because of its strongly hydrolysed form but it has been achieved in acidic conditions, either strong (up 6 M HCl) or mild (pH 1), with a very negative deposition potential in the latter case\(^1\). This presentation will report on the detection of antimonate ($\text{Sb(OH)}_6^{\text{-}}$) at a polycrystalline gold electrode by anodic stripping voltammetry in a wide range of pH. It will be shown that addition of cations (monovalent, divalent or trivalent), facilitate the electrochemical detection of $\text{Sb(OH)}_6^{\text{-}}$, irrespective of the solution pH. All tested cations (including Na, K, Ca, Mg, Sr, Y or La) improved the stripping Sb peak, although at varying degree depending on both their concentration and deposition potential. However, a common feature for the reduction of antimonate to occur, irrespective of the nature and concentration of the added cation, is a deposition potential that needs to be lower than that of the reduction of water (c.a. -1 V vs Ag/AgCl), suggesting that hydrogen evolution or the presence of nascent hydrogen may be involved in the reduction process of antimonate. Similar process of “cation mediated reduction” were reported earlier for the detection of other anions such as arsenate at neutral pH in presence of Mn ions\(^2\) or for nitrate reduction in presence of Cs or Na\(^3\). We propose that the underpotential deposition (UPD) of cations on the gold solid electrode forms positively charged adatoms that in turns, become adsorption site for anions such as antimonate, facilitating their reduction through possibly the reducing power of nascent hydrogen. From indirect observations made here by the stripping peak of antimonate, it appears that the UPD of cations such as Ca is facilitating the reduction of $\text{Sb(OH)}_6^{\text{-}}$ at potentials as high as -1.2 V, i.e. well above its standard reduction potentials. Although anion adsorption on solid electrodes has been extensively studied, UPD of halide and alkali-earth cations is barely known but seems to be a common process.


Design of Portable Sensor to Detect Pollutants in our Environment.

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Anthropogenic activity increases pollutant diversity in our environment. Therefore there is a need for developing simple methods for diagnosis of the target beneficial or harmful molecules in our environment. In electrochemistry, it is well known that performance of solid electrodes may be drastically altered by various processes such as adsorption of organic or inorganic species on the electrode, leading sometimes to the passivation of the electrode surface. This kind of irreversible process can be circumvented by using dropping mercury electrode with continually fresh Hg surface and new drop every few seconds. However, due to the toxicity of Hg and of technical inconveniences, colorimetric or spectrophotometric techniques are the most frequently used methods for long-term on-line analysis or for field measurements, despite the fact that they are less sensitive than electroanalysis. Our team has developed a new concept of device based on sampled-current voltammetry performed on an electrode array (figure 1).

![Figure 1: Description of the device: at the left the wafer with the three electrodes to create an electrochemical sensor, in the middle the electrochemical cell devised in the lab, at the right an example of the experimental result’s with the comparison responses between a single electrode analyse and an electrodes array analyse.](image)

In fact a single electrochemical measurement is performed independently and differently on each electrode in the array (figure 1). Each electrode plays a similar role than a dropping Hg electrode in polarography and the renewal of the electrode surface and of the solution in the proximity of the electrode is assured. With this concept, the value of the current can be multiplied by 10 or 100, which is particularly interesting for a portable device. However, the sensitivity of the method strongly depends on the affinity between the surface and the electroactive species and the selectivity is only obtained by its oxidation or reduction potential. The use of modified surfaces allowing the selective preconcentration of the pollutant on the electrode array should improve the performances of the sensor and allowed its use in different media. Consequently, we work on the development of reliable high sensitivity analytical methods to target hazardous molecules. The operating device and its application will be presented through the example of lead detection.

References
The characterization of polysaccharides in seawater accessed by electrochemical methods

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Polysaccharides (PS) are constituents of organic matter in seawater [1]. They are surface active (accumulate at different phase boundaries), complex copper( and other metal ions) ions and could give catalytic hydrogen evolution wave (catalytic peak) in electrochemical measurement which could serve for their analytical determination. Direct stripping of model PS placed in UV-irradiated seawater (pH~8) did not give any catalytic peak and an adsorptive transfer technique (AdT) [2] was applied in order to determine PS (Fig. 1). The electrolyte of choice to which the accumulated PS was transferred was acetate buffered sodium chloride solution (pH~5). Stripping was done by applying constant reduction current adjusted to chronopotentiometric mode.

Experiments were done with model sulphated PSs chondroitin sulphate, carrageenans, dextrane sulfate and nonsulfated PS dextran, having different structures and thus making different conformation in water solution. As model compounds for calibration of seawater samples microbial PS xanthan was used (Fig 2).

Polysaccharides are not the ligands that bind metal ions in a strong organic complex. The hypothesis that PS enable metal ions better bioavailability to phytoplankton by forming strong organic complexes, was not proved regarding copper ions, which otherwise are known to form very stable organic complexes. Due to high surface activity of PS and their accumulation at different phase boundaries / surfaces, the residence time of metal ions at these surfaces are prolonged and on that way PS enable phytoplankton to use the essential metal ions and other nutrients more efficiently.

References:
Review and recent developments of AGNES: a stripping technique for the determination of free metal concentrations

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The knowledge of the free metal concentration is key to understanding the bioavailability and toxicity of metals and micronutrients in environmental and biological systems. There is a limited number of techniques able to determine the free ion concentration, lacking sometimes selectivity, sensitivity or involving very complex interpretations. The electroanalytical technique AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has been specifically developed to determine directly the free metal concentration with a very simple interpretation [1]. The essential feature of AGNES is the attainment, by the end of a first stage, of an equilibrium situation, while the second stage aims at quantification of the accumulated analyte. The equilibrium potential can be selected according to a desired pre-concentration factor, so that free metal concentrations in the subnanomolar range can be measured.

AGNES has been typically applied with the standard hanging mercury drop electrode (HMDE), but other mercury-based electrodes [2] and non-mercury electrodes (Bismuth Film [3], vibrating gold microwire electrode VGME [4]) have been used. Different variants of the potential program have been tested: for the first stage and for the second stage (the analytical signal can be the diffusion limited current or the charge resulting from a potential pulse, a linear potential scan or stripping chronopotentiometry [5]). Validations included the Ion Selective Electrodes, the Resin Titration technique [6], stripping chronopotentiometry at scanned deposition potential SSCP, the Donnan Membrane Technique DMT [7] and Competitive Ligand Exchange Cathodic Stripping Voltammetry [8].

AGNES has been applied to synthetic and natural systems: soil extracts [7] and humic acid studies, sea water [2], estuarine water [8] and river water [5] (dealing with anomalous effects arising from low ionic strength), systems containing nanoparticles [9] and wines. Metals like Zn, Pb and Cd have been extensively considered with AGNES. Cu, In and Sn are also under study.

References

Acknowledgement - The authors thank all the co-workers in AGNES development along these years. Financial support from the Spanish Ministry (project CTM2013-48967) is also acknowledged.
Maximizing mechanistic information from DGT-plant studies

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When plants are grown in the complex medium of soils it is challenging to control variables so that the uptake mechanisms of toxicants and/or nutrients can be deduced. Direct measurements can be made of the free ion activity in soil solution and the potential of a soil to supply analyte under diffusion-limited conditions can be assessed using dynamic techniques, such as diffusive gradients in thin-films (DGT). When metal concentrations in plant shoots grown in soils with a wide range of metal concentrations were first found to correlate better with DGT measurements than free ion activities or concentrations in soil solution, it was thought that this provided evidence for uptake in these soils being controlled by supply rather than plant processes¹. Subsequently, it was appreciated that better correlations do not allow the assignment of a general mechanism², as illustrated by the study considered here³.

Radish was grown in 13 diverse soils that were unamended and also spiked with moderate and high concentrations of Ni and Cd. Metal concentrations were measured in the roots and shoots of the harvested radish and in soil solutions (c_{soil}) and in soils by DGT (c_E). Free ion activities (aM^{2+}) were calculated using WHAM from soils solution concentrations and measured soil characteristics. Comparisons of c_E and c_{soil} for Ni showed that the soils could be divided into two groups corresponding to appreciable and negligible supply from the solid phase. Amendment with a high concentration of Ni largely eliminated these distinctions between soils, possible by reducing complexation in solution, but more probably by providing a labile solid phase pool. Although there was a poor relationship between Ni in radish roots and either c_{soil} or aNi^{2+} in unamended soils, the soils with a low uptake by radish relative to c_{soil} or aNi^{2+} were those identified by DGT as having a diffusion only supply and some complexation in solution. By contrast Ni in radish was linearly related to c_E, demonstrating that DGT measurements mimic plant uptake and account for the difference between soils associated with resupply from the solid phase and complexation in solution. For soils amended with high concentrations of Ni, linear relationships were obtained for Ni in radish plotted against c_{soil}, aNi^{2+} or c_E, consistent with plant controlling uptake. These findings are consistent with the hypothesis that supply is likely to be controlled by diffusion at low metal concentrations and by the plant at high concentrations².

Metal in plants grown in all soils for all three amendments were plotted against either c_{soil} or c_E using customary log-log plots to span the concentration ranges. Each data set was fitted well by a single line, with little difference in correlation coefficients, illustrating how such an approach can fail to reveal mechanistic details.

References
Comparison between active and passive sampling POCIS for monitoring polar pesticides in Tra Vinh rivers (Mekong Delta)

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Tra Vinh is a coastal Vietnamese province in Mekong Delta with about 75 % of the land (175,550.38 hectares of agricultural land in total of 234,115.53 hectares of natural land) for agricultural use, especially paddy rice. The dams in Tra Vinh province have been built up to prevent the tidal saltwater intrusion with two important systems: Lang The and Tam Phuong. They are closed for about six months from December to June when the tide external salinity is usually ≥ 1 ‰. During this period all activities of living and agricultural production are carried out with uncirculated river water. Our studies aim to assess the environmental fate of polar pesticides as triazines (simazine and atrazine), phenylureas (diuron), carbamates (pirimicarb, carbaryl, carbofuran and isoprocarb), and phenoxyacetic acids (2,4-dichlorophenoxyacetic acid usually called 2,4-D) in Tra Vinh rivers. Beside the grab (active) sampling, the passive sampling with POCIS was applied to detect the analytes at trace concentrations and reduce the risk of missing potential contamination peaks by the accumulation and pre-concentration of analytes inside the receiving phase.

Firstly, our study focused on the development of analytical methods consisting of purification and preconcentration procedure with solid phase extraction using Oasis HLB that is also the solid sorbent placed in POCIS. The analytical method was performed on Waters ACQUITY UPLC/TQD with UPLC ACQUITY® BEH C18 column (100 mm x 2.1 mm, 1.7 µm). We obtained a high sensibility and robustness method for the dertermination of these analytes at trace levels in surface water (LOD < 0.003 µg.L⁻¹). Secondly, we performed the investigation on POCIS in laboratory by using appropriate models to determine the uptake rate (RS – L.day⁻¹) for each analyte. The time-weighted average (TWA) water concentrations (C₆) are calculated by the equation: C₆ = C₆ / M₆ = Rₛ x t, with C₆ (µg.L⁻¹) and C₆ (µg.g⁻¹) the analyte concentration in water and sorbent, respectively, M₆ the mass of the sorbent (0.2 g), and t time in day. In June and July 2015, samples were taken after the rice fields were sowed for 1 and 10 weeks. We found the presence of some herbicides as carbofuran, diuron, and especially atrazine and 2,4-D at different levels at 4 positions of Tra Vinh rivers: P1 at outside (about 0.5 km) and P2 at inside (about 1 km) from Lang The dam, P3 at inside (about 1 km) from Tam Phuong dam, and P4 at a small canal near the rice fields. For grab sampling the concentrations varied from 0.005 to 0.80 µg.L⁻¹. For passive sampling with 1 week exposure of POCIS at rivers, C₆ varied from 0.08 to 53.1 µg.L⁻¹ (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbofuran (Rₛ = 0.603)</th>
<th>Atrazine (Rₛ = 0.494)</th>
<th>Diuron (Rₛ = 0.369)</th>
<th>2,4-D (Rₛ = 0.052)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆ (µg.g⁻¹)</td>
<td>C₆ (µg.L⁻¹)</td>
<td>C₆ (µg.g⁻¹)</td>
<td>C₆ (µg.L⁻¹)</td>
</tr>
<tr>
<td>P2_July15</td>
<td>1.63 (5.4)</td>
<td>0.08</td>
<td>90.4 (1.9)</td>
<td>5.1</td>
</tr>
<tr>
<td>P3_June15</td>
<td>42.4 (9.8)</td>
<td>1.9</td>
<td>13.8 (9.9)</td>
<td>0.76</td>
</tr>
<tr>
<td>P3_July15</td>
<td>3.16 (4.4)</td>
<td>0.15</td>
<td>97.8 (3.5)</td>
<td>5.5</td>
</tr>
<tr>
<td>P4_July15</td>
<td>34.3 (5.9)</td>
<td>1.6</td>
<td>117 (4.4)</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Table 1: POCIS concentrations (C₆) after 7 days with % RSD (n = 3) and time-weighted average (TWA) concentrations

Our study, which showed the presence of atrazine and 2,4-D in Tra Vinh rivers, will further focus on their sorption behavior on sediments and colloids, and on their transport in surface and ground water.

References
Real-time X-ray Fluorescence in Probing Rhizosphere Processes Controlling Release and Losses of Phosphorus and Other Macronutrients

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Over the past decade, significant improvement in the tools and detection methods were made available to researchers and producers for improving estimates of crop nutrient requirements and fertilizer needs. Properly assessing soil nutrient status to provide supplemental inputs, if needed, is often made using various soil testing methods during the pre-plant period. However, options for monitoring and making real-time fertility adjustment needed in response to changing nutrient availability within the growing season have been limited, in particular for field soils amended with organic sources of nutrients or bio-fertilizers. Instrumental techniques include traditional methods of electrochemistry, radiological, atomic, and molecular spectroscopy. They are used to probe nutrient availability or gain an improved understanding of processes that control nutrient speciation, partitioning, and transformations occurring at the soil-water-plant root interface, and lastly, of plant uptake and assimilation.

Energy-dispersive X-ray fluorescence was evaluated and adapted for its potential as a soil and plant mineral nutrient sensor because of the rapid, element-specific, and non-destructive nature of the fluorescence analyses. Phosphorus (P) calibration curves developed for flag leaves of Zea mays showed that spatial distribution of foliar P (3.6, 4.2, and 5.3 g kg⁻¹) corresponded to field zones amended with animal manure at 0, 15, and 30 kg P ha⁻¹ for the past 18 years. Its significant correlation to leaf water content (r² = 0.94 and root mean squared error = 0.02) can be used to develop spectral calibrations and algorithms for specific crops to determine foliar P concentration and unbiased estimates of crop P status in real time. Since a simultaneous multi-elemental analysis was performed, corollary information was also obtained about the status of other minerals that could affect P availability (i.e., Ca, Fe, Al, etc.). Information about chemical interactions and nutrient balance could also be inferred to attain a more holistic knowledge of the plant nutritional conditions of the rhizosphere. Therefore, X-ray fluorescence methods may alleviate the technological shortcomings and information gaps about inorganic macronutrients status in plants and soils. These sensing methods can provide greater density of compositional measurements almost instantaneously, and improve the timeliness of the analytical information for precision nutrient management. The in situ fluorescence sensing system presents a new paradigm in nutrient management to insure the sustainability of crop production systems and the development of field-specific nutrient planning and management practices, while minimizing excessive fertilization, losses, and negative impacts on surrounding natural ecosystems.

References


Comparison of emerging techniques for Zn speciation measurements in a nutrient solution

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Speciation measurements of metals in complex solutions where different ligands are present are a demanding task. Conventional analytical techniques such as atomic absorption or atomic emission are not suitable for this purpose. Rather, it is necessary to develop analytical techniques able to measure not the total metal in solution, but the free fraction or the labile species. Investigations in this topic have resulted in the development of specific methodologies, including DGT (Diffusive Gradients in Thin films), DMT (Donnan Membrane Technique), PLM (Permeation Liquid Membranes) and ASV (Anodic Stripping Voltammetry), for metal speciation studies. More recently, AGNES (Absence of Gradients and Nernstian Equilibrium Stripping)² has been designed for free metal measurements.

We have developed new approaches for zinc flux monitoring associated to labile fractions based on Polymer Inclusion Membranes (PIMs)². Polymer inclusion membranes are a type of functionalised membranes similar to PLM. The designed PIMs basically consist of a base polymer, usually cellulose triacetate (CTA) or polyvinyl chloride (PVC), which provides mechanical strength to the membrane and a carrier (or extractant) to facilitate the selective transport for specific chemical species. Based on previous results, D2EHPA (di-2-ethylhexyl phosphoric) acid as extractant and PVC as polymer have been selected in our membrane composition to probe Zn, an essential element for plant nutrition.

We have applied different techniques (DGT, PIM, ASV and AGNES) for zinc speciation measurements in a hydroponic medium (half-strength Hoagland solution) where potato plants (Solanum tuberosum) where grown. The impact of the addition of organic ligands (humic acid and EDTA) is also considered. PIM and ASV fluxes are compared with the fluxes obtained with DGT and correlated with the free fraction of zinc measured with AGNES. Correlations between the amount of Zn accumulated in the plant and the free and labile fractions measured in the hydroponic media with the different techniques will be evaluated.

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Acknowledgement: Funding from the Spanish Ministry MINECO (projects CTM2012-39183 and CTM2013-48967) is acknowledged.
Electrochemical advanced oxidation processes: Application to the remediation of waters with organic pollutants

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This communication presents the application of electrochemical advanced oxidation processes (EAOPs) like electrochemical oxidation (EO), electro-Fenton (EF), UVA photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF) to the decontamination of organics from waters using undivided tank reactor or filter-press flow cells containing a boron-doped diamond (BDD) anode and an air-diffusion cathode. In EO, organics are destroyed by heterogeneous hydroxyl radical BDD(•OH) formed at the anode surface from water oxidation:

$$\text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD}(\cdot\text{OH}) + \text{H}^+ + \text{e}^- \quad (1)$$

In EF, the oxidation ability of H$_2$O$_2$, continuously generated at the cathode from reaction (2) is enhanced by adding Fe$^{2+}$ ion to the solution giving •OH in the bulk from Fenton’s reaction (3) at optimum pH 3.

$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad (2)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{•OH} + \text{OH}^- \quad (3)$$

Organics are then attacked by both, BDD(•OH) formed from reaction (1) and •OH produced from Fenton’s reaction (3). The PEF and SPEF processes involve the simultaneous irradiation of the treated solution under EF conditions by UVA light and sunlight, respectively. In these EAOPs, the mineralization of organics is enhanced by the higher Fe$^{2+}$ regeneration with more •OH production via Fe(OH)$^{2+}$ photolysis by reaction (4) and the photodecomposition of Fe(III)-carboxylate species by the global reaction (5).

$$\text{Fe(OH)}^{2+} + \text{h}^+ \rightarrow \text{Fe}^{3+} + \text{•OH} \quad (4)$$

$$\text{Fe(OOCR)}^{2+} + \text{h}^\nu \rightarrow \text{Fe}^{2+} + \text{CO}_2 + \text{R}$$

The high oxidizing ability of EO will be exemplified for the degradation of the herbicide atrazine, the drug omeprazole and the antimicrobial sulfamethazine in 100 mL stirred tank reactors with electrodes of 3 cm$^2$ area. The influence of key parameters like pH, applied current density and substrate concentration on the mineralization rate and mineralization current efficiency will be examined. Good mineralization degrees were obtained except for atrazine, which is transformed into cyanuric acid. Aromatic intermediates were detected by reversed-phase HPLC and generated carboxylic acids were identified by ion-exclusion HPLC. Final carboxylic acids were mineralized under the action of generated BDD(•OH), a fact that does not take place with heterogeneous hydroxyl radicals formed at the surface of other anodes like Pt.

The comparative EO, EF, PEF and SPEF degredations for the drug ibuprofen and the drug precursor α-methylphenylglycine will be examined in a 100 mL stirred tank reactor with electrodes of 3 cm$^2$ area. The influence of key parameters like pH, applied current density and substrate concentration on the mineralization rate and mineralization current efficiency will be examined. Good mineralization degrees were obtained except for atrazine, which is transformed into cyanuric acid. Aromatic intermediates were detected by reversed-phase HPLC and generated carboxylic acids were identified by ion-exclusion HPLC. Final carboxylic acids were mineralized under the action of generated BDD(•OH), a fact that does not take place with heterogeneous hydroxyl radicals formed at the surface of other anodes like Pt.

The scale-up of the SPEF method to a 2.5 L flow plant with a 20 cm$^2$ BDD/O$_2$-diffusion cell coupled to a 600 mL flat solar photoreactor will be further described. Solutions up to 200 mg L$^{-1}$ of TOC in 0.05-0.10 M Na$_2$SO$_4$ with 0.5 mM Fe$^{2+}$ at pH 3.0 and 50 mA cm$^{-2}$ were usually tested to obtain an almost total mineralization of the herbicide mecoprop, o-, m- and p-cresol. The SPEF process has also been performed in a 10 L flow plant with a cell of 90.3 cm$^2$ electrodes and coupled to a 1.57 L solar compound parabolic collectors (CPCs) photoreactor to treat the beta-blockers atenolol, metoprolol tartrate and propranolol hydrochloride. For this plant, a combined reactor equipped with a BDD/air-diffusion-Pt/carbon-felt cell gave low energy consumptions close to 250 kWh kg$^{-1}$ TOC for > 95% mineralization.

Finally, the characteristics of the degradation of atrazine using a hybrid method involving SPEF with a BDD/BDD cell and solar TiO$_2$ photocatalysis, as well as of a winery wastewater by coupling electrocoagulation and PEF with a BDD/BDD cell, will be discussed.
Transport of OMPs through FO membranes: influence of OMP and draw solute properties

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In this study, the transport of Organic Micro Pollutants (OMPs) through Forward Osmosis (FO) membranes is investigated. FO has been researched as a membrane process capable of treating highly polluted feed streams \cite{1}, streams which could contain OMPs. It is therefore important to study the fate of OMPs in FO systems as well \cite{2}.

In this work, the rejection of 27 OMPs with different physico-chemical properties was studied. The FO membranes of cellulose triacetate (CTA) were operated in AL-FS (FO) mode. 4 draw solutes (NaCl, MgCl\textsubscript{2}, Na\textsubscript{2}SO\textsubscript{4} and MgSO\textsubscript{4}) were tested at 5 concentrations, as well as simple diffusion (no salts present). In a separate set of experiments, the flux behaviour of the draw solutes was evaluated as well.

It was found that the draw solute influences OMP rejection through charge effects: neutral and anionic OMPs were better rejected by sulfate draw solutes, while cationic OMPs were better rejected by chloride draw solutes. Other draw solute effects were noted as well. For uncharged OMPs, the membrane permeability during diffusion was as high as during FO operation with chloride draw solutes, but was reduced when sulfate draw solutes were used. No relation was found between the draw solute permeabilities and OMP permeabilities. The draw solute permeability decreased in the following order: NaCl > MgCl\textsubscript{2} > Na\textsubscript{2}SO\textsubscript{4} > MgSO\textsubscript{4}. The hypothesis that a higher draw solute permeability hinders OMP transport is thus not supported by this study \cite{3}.

![Figure 1: Rejection of Diuron in function of water flux and draw solute](image1.png)

![Figure 2: Rejection of Sulfamethoxazole in function of water flux and draw solute](image2.png)

Certain OMPs showed a different permeability depending on the draw solute (e.g. fig.1), but this was not the case for every OMP (e.g. fig.2). Those OMPs whose membrane permeability were influenced by the draw solute, were predominantly smaller compounds in terms of molecular weight and surface area, showing an overall lower rejection. Susceptible compounds had an average molecular weight and surface area of 201 g/mol and 291 Å\textsuperscript{2} resp., compared to the average of 248 g/mol and 353 Å\textsuperscript{2} for all OMPs. It is therefore hypothesized that adsorption of certain draw solutes causes subtle structural changes in the membrane active layer. The permeability of relatively large compounds would not be impacted to a large extend, as transport through the membrane active layer of these compounds is strongly hindered in any case. The influence of structural changes would be larger on smaller compounds, with a size closer to the pores of the active layer.

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\item \cite{3} Xie, M et al. Comparison of the removal of hydrophobic trace organic contaminants by FO and RO, Water Research 46 (2012) 8
\end{itemize}
Hybrid sonolysis application as polishing step for removal of THMs generated from the drinking water treatment flow based on coagulation-flocculation, filtration and chlorination

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This paper emphasizes the possibility to use sonolysis (chemical oxidation based on active radicals generated during cavitation process) as polishing step in drinking water treatment flow for trihalomethanes (THMs) removal (concentrations over the admitted limit - 100 µg THM/l). Preliminary experimental tests were performed on synthetic water (deionized water and THMs dosage: trichloromethane, tribromomethane and bromodichloromethane) in order to establish the influence of THMs initial concentration, type of sonolyse system, ultrasonic irradiation time, ultrasonic energy and amplitude. Ultrasonic frequency was constant 20 kHz.

Four sonolysis systems were tested both for synthetic and real surface treated water: direct sonolysis (US), US + H₂O₂, US + H₂O₂ + Fe (Fenton sonolysis), US + H₂O₂ + Fe + UV (low pressure mercury lamp 250 - 400 nm). The variation domains of the main process parameters were as following: THMs concentrations 310 ÷ 3600 µg/L, sonolysis time 1 ÷ 60 min., ultrasonic energy 2x10⁶ J - 6x10⁶ J, ultrasonic amplitude 20 ÷ 80%, oxidant dose 0.6 ÷ 2.1 g H₂O₂/L, catalyst dose 0.25 ÷ 2 mg Fe²⁺/L.

The sonolysis tests with surface water were performed after the raw water was treated according to classical scheme: coagulation with Al₂(SO₄)₃ - 2 mg Al/L dose, 10 minutes stirring, flocculation with Romanian flocculant based on starch and acrylamide (containing silver) 0.1% d.wt., 2 ml/L dose, chlorination. Total THMs content was ~350 µg/L. These reagent doses and reaction times were established to be optimal based on previous research experiments.

The best results for the sonolysis test were obtained in the following experimental conditions:
- direct sonolysis: pH 7, time 30 min., energy 8x10⁶ J, amplitude 25%;
- hybrid sonolysis US + H₂O₂: similar with direct sonolysis + 1.7 g H₂O₂/L;
- hybrid sonolysis US + H₂O₂ + Fe: similar with previous system + 1 mg Fe/L;
- hybrid sonolysis US + H₂O₂ + Fe + UV: pH 7, sonolysis time 30 min., UV irradiation time 30 min., 1.7 g H₂O₂/L, 1 mg Fe/L, energy 8x10⁶ J, amplitude 25%, iron catalyst and oxidant have put together in the photolytic reactor, after direct sonolysis phase;

These working conditions make possible to compare THMs removal efficiencies for different sonolysis systems:

<table>
<thead>
<tr>
<th>No.</th>
<th>Sonolysis system</th>
<th>η THM, %</th>
<th>η Σ THM, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>US</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>US + H₂O₂</td>
<td>70</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>US + H₂O₂ + Fe</td>
<td>82</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>US + H₂O₂ + Fe + UV</td>
<td>63</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 1: THMs removal efficiencies in different sonolysis systems

Experimental results showed the evolution of THMs removal depending on sonolysis system:
- direct sonolysis (US) 56% < sonolysis and hydrogen peroxide (US + H₂O₂) 59% < Fenton sonolysis (US + H₂O₂ + Fe + UV) 63% < Fenton sonolysis (US + H₂O₂ + Fe) 73% emphasizing that bromoform are more difficult to remove compared to other.

Acknowledgement - This work was supported by a grant of the Romanian National Authority for Scientific Research – PN2: 64/2012 –Project FLAMIR and Programme Nucleu – Project PN 09-13 03 16
Catalysis and kinetics of diesel soot oxidation over nano-size perovskite catalyst

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Diesel engines are important power systems for on-road and off-road transportation. Most heavy-duty trucks, buses, ships, locomotives and other machineries are driven by the diesel engines due to the long record of reliability, high fuel-efficiency and high torque output. However, diesel engines emit significant amounts of particulate matter (PM/soot/smoke/black carbon-BC). Emission of PM has negative impacts: locally causing pollution of air, water and soil, soiling of buildings, reductions in visibility, etc.; regionally altering monsoon circulation; and globally increasing the earth temperature. BC is the most strongly light–absorbing component of soot and compounds global warming effect of CO\(_2\) [1]. Therefore, stringent Euro 6/VI regulations for light duty and heavy duty vehicles respectively with catalysed diesel particulate filters (DPF) have largely reduced PM emissions in some parts of the world; however, for remaining parts of the world as well as for seagoing-ships and trains, the implementation of improved DPF is still a compelling challenge for catalyst developers. The key challenge is to find a catalyst that decreases the combustion temperature of PM (> 600°C) within the range of diesel exhaust (150-450°C) [2]. The present work reports a comparative study of perovskite catalysts prepared by sol-gel (SG) and reactive grinding (RG) methods for the soot oxidation. The optimal formulated perovskite, La\(_{0.9}\)Sr\(_{0.1}\)Co\(_{0.5}\)Fe\(_{0.5}\)O\(_3\) (Cat-D) prepared by RG with ZnO additive and reactively calcined (RC) in a 4.6%CO-air mixture, exhibited the highest surface area (94.8 m\(^2\)/g), smallest crystallites (8.4 nm) and the best activity for diesel soot oxidation initiated at ~208°C, reached a peak at ~276°C and completed at 318°C.

Catalysts were characterized by N\(_2\)-sorption, XRD, XPS and SEM-EDX. Diesel soot oxidation was studied in a tubular reactor under following conditions: 110 mg of soot-catalyst mixture of ratio (1/10) under tight contact, air flow-rate of 150 ml/min, heating rate of 1°C/min from ambient to the temperature of total soot oxidation and at atmospheric pressure. The oxidation products CO and CO\(_2\) were analyzed by online GC equipped with porapak q-column, methanizer and FID detector.

The high activity of Cat-D may be related to its unusual characteristics arisen from RG and RC that the severe mechano-chemical deformation during ball-milling leads to fractures and cold welding, in addition to oxygen deficient structure produced by RC resulting high density of active sites in nano-size catalyst. Cat-D has good thermal stability found in a repeated cycles of soot combustion experiments. Thus, Cat-D shows potential as a cost effective catalyst for use in the passive regenerative DPF for a secure and sustainable environment.

Design of such a DPF requires rate of catalytic soot oxidation [3]. The kinetics of air oxidation of real diesel soot over cat-D under isothermal condition is reported in the present paper. Kinetics data were collected under the conditions of free heat and mass transfer limitations in a specially designed mini-semi-batch reactor under above mentioned conditions. In order to determine the kinetic model, activation energy and Arrhenius constant of the oxidation with high air flow rate, pseudo first order reaction was assumed. The kinetics for soot oxidation in the temperature range 325-355°C can be represented by the following rate expression:

\[
\text{Rate (r)} = 6.46 \times 10^{10} \times \exp (-101.08 /RT) \text{ (m) g soot/g cat.s}
\]

The activation energy was found to be 101.08 kJ/mol, which is the least compared with the values reported in the literature for soot oxidation over different catalysts.

References


Acknowledgement- The authors are gratefully acknowledging the financial support given for the project by the Department of Science and Technology, India under the SERC (Engineering Science) project grant DST No: SR/S3/CE/0062/2010.
Performances of bioelectrochemical technologies for energy passive wastewater treatment

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Until now wastewater treatment was an energy-consuming technology (around 50 kWh per year per inhabitant). The energy cost for the wastewater treatment represents 23% of the public energy use of a municipality [1]. Attitudes, economic issues and environmental challenges are changing and future technologies of treatment are now considering wastewater as a resource rather than a waste to be treated. In this light of valorisation, the bioelectrochemical technologies allow to recover a significant part of the chemical energy contained in the wastewater by the action of electroactive bacteria catalysing the oxidation of soluble organic substances on biocompatible electrodes. The flow of electrons generated by the electroactive bacteria can be dispersed in the case of energy passive treatment (microbial electrochemical snorkel [2]) or valued in the form of electrical energy (microbial fuel cell) or hydrogen (microbial electrolysis) for energy positive treatment (Figure 1).

Figure 1: Description of the bioelectrochemical technologies evaluated for wastewater treatment

The removal of the total organic load (COD) from raw urban wastewater and acetate enriched wastewater was studied using different bioelectrochemical technologies (BET): microbial fuel cell (MFC), microbial electrolysis (ME), and microbial electrochemical snorkel (MES). COD removal with the different bioelectrochemical technologies was compared using optimized carbon fibers based microbial anodes already working at steady state rate of oxidation. Optimization of microbial anodes consisted of immersing a microbial anode already colonized with electroactive microorganisms together with a second polarized clean electrode resulting in the formation of an electroactive biofilm on the clean electrode that became more effective than the initial one. This strategy multiplied the current provided by the second microbial electrode by a factor ranging from 2 to 20 in respect to the initial one.

The combination of polarizing the electrode and using as inoculum a pre-colonized electrode with electroactive microbial species had a very positive effect on improving the performance and the reproducibility of microbial anodes. Enrichment in electroactive population on second electrodes was highlighted based on the analysis of the biofilms microbial diversity (16s RNA pyrosequencing technology) and the redox properties of the microbial anodes (cyclic voltammetry analysis).

The comparative study using microbial anodes in different configurations of BET for the treatment of wastewaters validated the MES concept since the MES process ensured about 75% of wastewater COD removal in less than 24 hours as well as a “short-circuited” MFC. In conclusion, the MES technology, which aims at maximizing the reaction rates by elimination of current generation, provided degradation performance far higher than the MFCs that operated at optimum power. This demonstration opens a new route for the design of extremely simple bioelectrochemical devices for wastewater treatment.

References
Mixed-Metal Semiconductor Anodes for Electrochemical Water Splitting and Reactive Chlorine Species Generation: Implications for Electrochemical Wastewater Treatment

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A procedure for the preparation of semiconductor anodes using mixed-metal oxides bound together and protected with a TiO₂ nanoglue has been developed and tested in terms of the relative efficiencies of the oxygen evolution (OER), the reactive chlorine species evolution (RCS), and the hydrogen evolution (HER) reactions. The composition of the first anode is a Ti metal substrate coated with IrTaOₓ and overcoated with TiO₂ (P₂₅) that was mixed with TiO₂ nanogel, while the second anode consists of a Ti metal substrate coated with IrTaOₓ and an overcoating layer of La-doped sodium tantalate, NaTaO₃:La. The experimental efficiencies for water splitting ranged from 62.4% to 67.5% for H₂ evolution and 40.6% to 60.0% for O₂ evolution. The corresponding over-potentials for the Ti/IrTa-TiO₂ and Ti/IrTa-NaTaO₃:La anodes coupled with stainless steel cathodes of the same dimensions were determined to be 437 mV and 367 mV for the OER, respectively, and 239 mV and 205 mV for RCS, respectively. The preparation procedure described herein should allow for easier production of large-surface area anodes at lower costs than standard methods.
Bacterial Biofilm formation on carbon electrodes under influence of an electric field

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Capacitive deionization (CDI) is an energy-efficient promising technology to demineralize water electrochemically by applying an electrical potential difference over two carbon electrodes. Nevertheless, the CDI electrode often suffers from biofouling, which reduces its electrosorption ability and increases energy consumption. The present work is aimed at investigating biofilm formation under the influence and the absence of an electric field applied to carbon/graphite electrodes. The assessment of biofilm formation of Pseudomonas aeruginosa PAO1 to the Papyex and carbon aerogel was measured using a single channel flow cells. The samples were visualized using a confocal laser scanning microscope (CLSM) and the biovolume, average thickness and roughness coefficient of the developed biofilms were determined. The flow-cell experiments in the absence of an electric field demonstrated a slightly more pronounced biofilm formation on carbon aerogel in comparison to Papyex graphite sheet. The carbon aerogel surface provided less favourable conditions for biofilm proliferation than Papyex graphite due to its higher hydrophilic nature and presence of charged group. Further, the metabolic activity was hindered in the presence of suspended carbon aerogel dust (NTU 1260) as detected with an XTT colorimetric assay. Biofilm growth experiments in the presence of an electric field were carried out potentiostatically in a ‘two electrode electrochemical flow cell’ using both Papyex and carbon aerogel as working electrodes, while Indium tin oxide (ITO) coated glass was used as a transparent auxiliary electrode with a Platinum strip as the current collector. The effective potential window of the different working and auxiliary electrodes were determined by cyclic voltammetry (CV) at a range between -0.9 V to +0.9 V. Electrochemical flow cell experiments showed the impact of the applied electric potential on the bacterial biofilm growth. More biomass of live bacteria was found at open circuit condition compared to the electrodes at electrically polarized conditions. At positive potentials (at 0.3 V and 0.6 V, decreased at 0.9V), more biofilm was developed compared to negative potentials, probably due to electrostatic attraction. However, more dead cells were observed with positive applied potential (Figure 1). The lower cell viability in the positive potentials was probably due to the adverse effect of peroxide generation on the surface, which provided bactericidal effect. Dihydrorhodamine 123 was applied to trace generation of reactive oxygen species (ROS) by the biofilms and generation of ROS were detected. We suggest that cellular stress, induced by ROS, inhibited biofilm growth at both extreme negative and positive potentials (-0.9 V to +0.9V). The overall study indicated operating CDI at higher applied potential could be helpful to mitigate biofouling on the carbon electrodes.

Figure 1: Calculated cells biomass by COMSTAT after 36 hours of biofilm formation in an electrochemical flow-cell with 10% LB medium.
Transformation and products of organic micropollutants with the presence of humic substance in water during enzymatic catalysis

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Due to the potential damage on human health and the environment, the transformation and products of micro-pollutants during water treatment have attracted great concerns. Enzyme catalysis is a potential technology to remove micro-pollutants from water due to its high reactivity and selectivity [1-3]. However, humic substance (HS) mostly coexist in natural waters. It is a challenge to explore the transformation and products of micro-pollutants with the presence of HS.

We herein investigated the fate of transformation products of captopril in the presence of model humic constituents during laccase catalysis. After 1 h reaction, conversion of captopril ranged from 75% (syringic acid) to 96% (P-coumaric acid). Using UPLC-Tof-MS spectrometry, products were analyzed and reactions were proposed. The results indicated that conjugate quinones were formed by 1,4-nucleophilic addition of sulfhydryl group to quinones from humic constituents, and captopril likely attack the para position of humic constituent with strong electron withdrawing group and underwent nucleophilic substitutions. Notably, a second conjugate addition may continue occur on ortho-quinones generating di-substituted products. Stability assessment experiments revealed that cross-coupling products with para- and dimer- quinones were less stable than ortho- and mono- ones in acidic condition. The model humic constituents with individual functional groups showed significant differences of reaction pathway and reversibility. These findings are useful for understanding the mechanism of micro-pollutants removal by using the enzymatic catalysis and could eventually lead to the development of novel methods to control micro-pollutants and other contaminants.

Figure 1: Schematic overview of possible reaction mechanisms for covalent bonding of thiol drugs to organic matter in the presence of laccase.

References

Acknowledgement - The authors thank the support from the National Natural Science Foundation of China (Grant No. 51378487) and Youth Innovation Promotion Association, CAS.
New materials as electrodes for capacitive energy production

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Although their implementation has been relatively recent [1], interest in clean energy production and water deionization has grown almost unstopably, because the feasibility of these techniques is well demonstrated. In this contribution we will focus specifically on energy production, considering three approaches, generically known as capmix (capacitive mixing) techniques. In all of them, high-capacitance carbon electrodes are used but they differ in the way in which the electrodes are charged and discharged for energy extraction. In CDP, the Donnan potential of cationic or anionic membranes coating the carbons are used for spontaneously producing potential differences between the electrodes. A similar technique (SE or soft-electrodes), uses the potential difference generated by simply coating the active carbon films with cationic and anionic polyelectrolytes. Finally, in CDLE bare materials are used, and an external power source is used for charging, subsequently disconnected for the production step (Figure 1). Contrary to the previous ones, the cycle is productive in half of its extension. This makes materials selection even more critical in this case.

The amount of power obtained depends critically on the experimental design. To date, the highest values are associated to CDP, although SE seems to be close to the latter [2]. Figure 1 illustrates the large open circuit values which can be achieved by this technique; compare it to the lower voltage rises accessible to CDLE, although the cycles can be implemented for obtaining above 10 mW/m², using untreated activated carbons.

![Capmix cycles](Figure 1)

In this communication, we will test the possible improvements that can be reached by selecting different carbon materials for CDLE and SE, including carbon nanotubes, graphene or graphene oxide and hyperarchically porous carbons [4].

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Acknowledgement: The authors thank MINECO (Spain) and FEDER Funds (EU) for financial support through project FIS2013-47666-C3-1-R.
Adsorption of Effluent Organic Matter by Polycation-Clay Composite Sorbents: Effect of Polycation Configuration on Pharmaceutical Binding

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One of the complexities which water technologies face is treating low concentration of emerging micro-pollutants, such as pharmaceuticals, in the presence of dissolved organic matter (DOM), a heterogeneous mixture of relatively large soluble organic compounds. In the current study, new polycation-clay composites based on the adsorption of quaternized poly-4-vinylpyridine to clay were developed and tailored as sorbents for DOM and micro-organic pollutants. The aim was to unveil the effect of polycation configuration at the adsorbed state on composite functionality i.e., binding abilities. Polycation configuration at the adsorbed state, as trains and as loops and tails, was controlled by three parameters 1. solution ionic strength 2. polycation concentration 3. polycation charge density. Composite micro- and nano-structure was characterized by zeta potential, FTIR, X-ray diffraction and thermal gravimetric analyses (TGA). The filtration of DOM from treated wastewater effluent (EfOM) was more efficient by composite columns, approximately 3-fold higher, than by the granulated activated carbon (GAC) columns. We attribute this high removal mainly to electrostatic interaction between the positively charged composites (zeta potential 40 mV) and the negatively charged components of EfOM (zeta potential -20 mV). Although EfOM removal by filtration columns was not affected by polymer loading or configuration, it is reasonable that a loops and tails configuration will be beneficial for the removal of the smaller micro-organic pollutants which are within the size range of polycation loops and tails. Therefore, the removal of pharmaceuticals, diclofenac, gemfibrozil and ibuprofen from tap water or from EfOM by the composites, with a dominant train configuration (Comp Train) or with a dominant loops and tails configuration (Comp L&T), was tested. The removal of the pharmaceuticals from tap water or from EfOM by the Comp L&T was significantly higher than by the Comp Train, even upon normalizing to the polymer loading. The removal by both composites was obviously higher from tap water (EC=0.75) but the reduction in removal from EfOM (EC=1.5) was not dramatic indicating that the interactions of the anionic pharmaceuticals with the composites are not only electrostatic. Furthermore, this degree of reduction in pharmaceutical removal by the Comp L&T was smaller than the degree of reduction by the Comp Train. These results support our hypothesis that a loops a tails configuration offers beneficial binding sites for micro-pollutants and may explain our previous observation that the filtration of micro-pollutants in the presence of DOM by the GAC columns was reduced, while the removal by Comp L&T columns was not compromised and remained high²,³.

References
Prediction of the effects of competitive adsorption in the dye removal from wastewater by layered double hydroxides: competition between anionic Orange-type dyes and inorganic divalent anions

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One of the most important challenges inherent to the sorption-based technology for in situ treatment of pollution is related to the complex composition of the wastewater effluents. The removal performance of a given sorbent is obviously affected by the presence of other solutes which can enter into competition with the main pollutant component. Competitive adsorption is thus a phenomenon, which should be studied in order to predict the real efficiency of the removal technology.

In the present study, competitive adsorption between between anionic Orange-type dyes (Methyl Orange, Orange II, Orange G) and three inorganic anions (HPO$_4^{2-}$, SO$_4^{2-}$, CrO$_4^{2-}$) onto Mg-Al Layered Double Hydroxide (LDH) from bi-solute aqueous solutions has been studied in view of potential application in dye removal from textile wastewater effluents.

In the first stage, the individual solute affinities for the LDH sample were inferred from the calorimetry measurements of the cumulative enthalpy of displacement in single-solute systems and decomposed from theoretical results obtained by Monte Carlo calculations.

In the next stage, the individual and composite adsorption isotherms from bi-solute aqueous solutions were determined by solution depletion technique and supplemented by XRD studies on the well-defined sorption systems. Based on the shape of the individual adsorption isotherms for a dye and inorganic anion, it was possible to distinguish three different competition schemes exemplified in Figure 1.

![Examples of individual adsorption isotherms for dye anions (circles) and inorganic anions (triangles), as well as composite adsorption isotherms (stars), plotted as a function of the concentration of the dye component in the equilibrium bulk solution: Methyl Orange + SO$_4^{2-}$ system (Type I), Orange G + CrO$_4^{2-}$ system (Type II), Orange II + HPO$_4^{2-}$ system (Type III); the vertical dotted line is used to indicate the theoretical anion exchange capacity (AEC) of LDH [1]](image)

The bi-solute systems studied in the present work were ascribed to one of these three categories depending on the individual solute affinities for the LDH sample and their overall contents in the system, as expressed by the molar ratio between dye and inorganic anion. The order of effectiveness of the inorganic anion in depressing the retention capacity of Mg-Al-LDH towards a given dye was also established.

Reference
Effect of ageing on biochar properties and intrinsic contaminant composition

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Biochar has gained growing attention to increase the sustainability of remediation strategies for soils and sediments. After biomass pyrolysis, biochar exhibits a high sorption potential for organic and to some extent also for inorganic contaminants. It is well accepted that ageing processes change biochar properties. For instance, ageing may modify the elemental composition, porosity and the intrinsic contaminant contents and availability of, e.g., polycyclic aromatic hydrocarbons (PAHs) and heavy metals. Some of these changes may affect the long term impact of biochar application, and remain poorly understood.

Oxidative ageing processes may be simulated, and Cross & Sohi [1] proposed an approach to artificially age biochars by thermal oxidation with H₂O₂. Furthermore, Flores-Cervantes et al. [2] but excluding one study, conclusions relied solely on qualitative results. We incubated 13 different types of CNTs and subjected them to enzymatic oxidation with horseradish peroxidase and concluded that the analytical methods commonly employed for studying degradation of CNTs did not have the sensitivity to unequivocally demonstrate degradation of these materials. To obtain unambiguous results with regard to the biotransformability of CNTs in the horseradish peroxidase system we incubated: (a) showed that highly stable carbon materials, such as carbon nanotubes, can be partially degraded by enzymatic oxidation with horseradish peroxidase. This enzymatic ageing approach has not been previously applied to biochars, but may provide additional insight into environmental ageing processes. However, a general difficulty of artificial aging methods is that changes in the properties of artificially aged biochars may not be representative of changes caused by naturally occurring processes, and a comparison with naturally aged biochars is rarely possible.

In this study, the influence of ageing on biochar properties and intrinsic contaminant composition was investigated by comparing five biochars before and after artificial aging with H₂O₂ thermal oxidation. For one of the biochars, a naturally aged biochar could be obtained from an agricultural field site that was treated with biochar in 2011 by Karer et al. [3]. The respective biochar (stored in a dry and dark room) was additionally aged by enzymatic oxidation with horseradish peroxidase for comparison of representativeness of artificial ageing approaches. The biochars were characterized, including elemental composition and N₂ as well as CO₂ physisorption derived surface area and pore volume. Total PAHs content and heavy metal content were measured for all biochars and a contaminant trap approach [4] was applied to investigate the effect of ageing on the (bio)accessibility of PAHs.

Overall, total and (bio)accessible EPA 16 PAH contents ranged 4.05 - 22.59 mg/kg and 0.26 - 10.21 mg/kg, respectively. With ageing, contaminant contents tended to decrease, whereas the O-content increased. Results showed that (i) artificial ageing is a useful tool to investigate changes in biochar properties, but the representativeness of applied ageing methods must be further investigated, as artificially aged biochars showed different physico-chemical properties in comparison to naturally aged biochar, (ii) ageing can affect contaminant concentrations and PAHs accessibility, and (iii) the risk of biochar being a contaminant source appears to decrease with ageing for both artificially aged biochar and naturally aged biochar.

References:
Advanced experimental techniques to probe environmental interfacial processes

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The early stages of mineral nanoparticle nucleation and growth exert crucial influences on the sorption and transport of aqueous toxic species originating from both natural and anthropogenic sources. Homogeneous and heterogeneous nucleation often occur simultaneously, making it difficult to sort out whether toxic species are transported as sorbed or coprecipitated species on/within nanoparticles. Furthermore, once the nanoparticle is formed, transported and deposited, isotopes of the particle constituents can further interact with the mineral nanoparticle leading to an “isotopic signal” affected by early diagenesis.

Here a variety of techniques will be discussed that help putting some light onto these questions. Recent developments in X-ray scattering techniques such as Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) have been used to follow in situ heterogeneous nucleation and growth of mineral nanoparticles from solution, to identify dominant nucleation and growth mechanisms (Jun et al. 2010) and to quantify interfacial energies (Fernandez-Martinez et al., 2013). The effect of surface hydrophobicity vs. hydrophilicity on the energy barrier for heterogeneous nucleation can be evaluated by following nucleation on thin films coatings terminated by –COOH and/or –SH reactive sites (Dai et al, submitted 2016). Once formed, the kinetics of particle interactions with toxic ions can be followed by in-situ time-resolved XRF, in conjunction with EXAFS spectroscopy and PDF analysis of HEXS data. This allows the identification of the dominant sorption mechanisms, which for instance in an oxyanion/LDH interaction may shift from LDH-edge complexation to anion exchange, and finally to coprecipitation. Finally the very dynamic nature of these nanoparticle surfaces can now be probed by isotope exchange, modelled by metadynamics molecular simulations and even compared to field data. Chemical reactions occurring at the nanoparticle–water interface probed by the above techniques are shown to be controlled by a nanometer thick interfacial layer whose properties may deviate from those of the respective nanoparticle bulk, before and after reaction with a toxic species.

We will illustrate this by looking at a variety of field environmental observations (e.g. paleoenvironmental proxies), technological (e.g., concrete or scale, smart packaging, fillers in synthetic resins, and pharmaceutical formulations) and nanotoxicological issues.

References
The electrosorption process for energy generation

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Where solutions of different composition come together, energy is available. For instance, in the situation of a river discharging into the sea, power equivalent to a two hundred meter drop of the river can be generated. This so-called “Blue Energy” is a substantial clean renewable energy source. The challenge is to develop technology that is able to harvest this source in a clean, efficient and cost-effective way.

When two different solutions are directly mixed, the energy is directly dissipated as mixing entropy and no energy can be harvested. The basis of any technology is therefore selective mixing, where either the salt is transferred from the concentrated to the dilute solution, or water is transferred from the dilute to the concentrated solution.

There are several technologies available for generating energy from mixing two solutions. Pressure Retared Osmosis and Reverse Electrodialys are most advanced in development and both have been tested at pilot scale.

Electrosorption using porous electrodes is an attractive alternative process for this type of energy generation. The porous electrodes can be made selective for ion adsorption via applying either an electrostatic potential, a fixed surface charge, or a membrane. Electricity is directly produced and a secondary converter like a turbine or electrode reaction is not needed.

The state of the art will be discussed together with challenges ahead and new applications like generating energy from CO2-emissions.
Investigating the impact of ocean acidification on the speciation of iron - a combined experimental and modeling approach.

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Increasing atmospheric concentrations of CO₂ are likely to result in a decrease in surface ocean pH of approximately 0.3-0.5 pH units by the end of this century. Such a decrease in ocean pH will have an impact on the speciation of trace metals, and potentially change the availability of metals to marine phytoplankton. A change in the speciation of iron is particularly critical, as iron limits ocean productivity in approximately one third of the open ocean. Here we present experimental results from the determination of iron speciation at pH 7.91, 7.37 and 6.99 (expressed on the total pH scale) in 20 surface water samples collected from the North West European Shelf. We titrated seawater samples with iron and measured the concentration of an added competing iron complex - iron(1-nitroso-2-napthol) - by adsorptive cathodic stripping voltammetry. We model our results using non-ideal competitive adsorption in Donnan like gels (NICA-Donnan model), assuming that marine dissolved organic matter is composed of fulvic acid like material. Generic NICA-Donnan parameters were applied within the framework of the software program visual MINTEQ and the iron(1-nitroso-2-napthol) concentrations calculated and compared to concentrations measured at different pHs. We found that an inert iron fraction with kinetically inhibited dissolution was required in order to approximate the trends observed in our titrations. We utilized the approach to investigate changes in iron speciation at atmospheric pCO₂ of 280 (preindustrial), 400 (present day), 900 and 1900 µatm.
Redox reactivity of Fe(II) sorbed on smectites: U(VI) reduction

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The understanding of Fe(II)-U(VI)-clay ternary system is necessary to mitigate the future possible risk in U polluted subsurface and to ensure long term stability of U at underground waste disposal sites. We studied the reactivities of Fe(II) sorbed on three Ca-exchanged smectites viz. Fe-free montmorillonite (MONT), Fe-poor (2.6 wt.%) montmorillonite (Fe-MONT) and Fe-rich (25.8 wt.%) nontronite (NAu-2) in reductive transformation of U(VI) at pH 6.0 (± 0.2) under a CO2-free anoxic (O2 < 1 ppmv) condition using combined wet chemistry, X-ray absorption and 57Fe transmission Mössbauer spectrosocopies.

The sorption of Fe(II) onto clays increases in the order MONT < Fe-MONT < NAu-2 whereas removal of U(VI) from aqueous solution by Fe(II) sorbed clays follows the order: Fe(II)/Fe-MONT < Fe(II)/NAu-2 < Fe(II)/MONT. The analysis of ULIII-edge XANES spectra suggests a partial reduction (~14% of the total sorbed amount) of U(VI) by Fe(II)/MONT whereas no reduction is noticed in presence of Fe(II)/Fe-MONT and Fe(II)/NAu-2 after 72 h (Fig. 1). The detection of a neighbouring U-atom in Fourier-transformed EXAFS suggests the formation of amorphous schoepite-like surface precipitates on Fe(II)/MONT after 24 h which however does not affect U(VI) reduction. The Mössbauer data reveals that 10% of the total sorbed Fe(II) was oxidized in presence of MONT before and 6% after U(VI) addition. The mechanism of U(VI) reduction has been suggested by considering the reactivities of Fe(II) sorbed on oxidized and reduced strong sites of MONT. The non-reactivity of Fe(II)/NAu-2 towards U(VI) reduction may presumably be linked to the inter-valence charge transfer (IVCT) between surface Fe(II) and tetrahedral Fe(III) in NAu-2. Unlike other two clays, Fe-MONT exhibits neither IVCT nor surface catalysis in U(VI) reduction. This study demonstrates that reduction capacity of specifically sorbed (surface complexed) Fe(II) strongly depends on the nature of mediating clay surface and may not be always considered as “universal reductant” for U(VI).
Iron nanominerals in mining environments: formation, stability and reactivity

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Mining and processing of mineral ores constitute major sources of contamination in soils, sediments and aquatic systems. The presence of secondary iron and aluminum minerals can be considered of great importance in these areas, since they are naturally occurring scavengers for most of the contaminants present. The formation, nature and composition of the iron nanominerals present in these mining areas is determined by the ore mineralogy, weathering conditions and the physico-chemical characteristics of the aqueous phase. Generally, formation of schwertmannite, or other iron oxyhydroxyulfate phases, is favoured at the more acidic pH conditions, while nanoferrihydrite is commonly formed at neutral pH conditions [1]. Changes in the nature of the mineral surfaces occurring in mining areas will affect the adsorption of trace metals and metalloids and therefore may prevent or enhance the leaching process and the contamination of ground and surface waters [2,3]. It is important to be able to accurately predict the reactivity of these nanominerals to target species of environmental interest and how this reactivity may affect their medium to long-term thermodynamic stability.

In this presentation, the chemical behaviour of iron nanominerals present in acidic and sulphate-rich mining systems will be discussed. Mixtures of varying proportions of schwertmannite, jarosite, goethite and ferrihydrite particles collected at sites affected by acid mine drainage were analysed and synthetic analogues were also studied for comparative reasons. The reactivity of these nanominerals was established in the presence of arsenic, copper or chromium. Factors that may affect their reactivity and stability, such as the amorphous or crystalline character of the mineral phase, pH, time, and presence of competing ions, will be analysed. Thermodynamic description of the surface reactivity was also assessed using surface complexation models, which allows to elucidate the mechanism controlling ion adsorption and to calculate the contribution of surface adsorption and anion exchange reactions. The main objective is to determine the ability of the iron nanominerals to reduce the concentration of these inorganic contaminants from the aqueous solution and to improve our understanding of the solid/solution processes in mining environments.

References

Effect of aluminum substitution on the Pb(II) adsorption on goethite and CD-MUSIC modeling

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Iron oxides, such as goethite, are common minerals in soils and aquatic environments. The sorption of heavy metals or other elements by iron oxides is important since it will significantly control their concentration and speciation in complex geochemical systems. But Goethite (α-FeOOH) often contains Al as an isomorphous substitution, it rarely exist as pure phase in natural environments. Aluminum substitution on goethite can change the crystallographic, mineral and chemical properties of goethite, while few result of surface charge characteristics of the isomorphous substitution of aluminum on goethite are reported.

Then, in our study a series of Al-substituted goethite (G-0, G-10 and G-15) were synthesized and characterized. Aluminum substitution make the crystal structure of Al-goethite more stable than pure goethite and decrease the fraction of ratio between the (110) faces and the (021) faces. With the increasing of the amount of Al substituted, the d value and SSA of goethite decreased, while OH content increased gradually. The PZC of sample G-0, G-10 and G-15 changed insignificantly, but the surface charge showed an upward tendency. The charge density of sample G-10/15 by MUSIC model calculation coincides with the experimental value. Furthermore, from the Pb isotherm adsorption result, that the Pb adsorptions capacity showed a decline tendency with the amount of Al substituted increase was found. There exist two deprotonated Pb complexes ([Fe(Al)OH]2 Pb, [Fe(Al)OH]2 Pb[Fe(Al)3 O]) and two protonated complexes ([Fe(Al)OH]2 PbOH, [Fe(Al)OH]2 PbOH[Fe(Al)3 O]) on Al-substitution goethite by the CD-MUSIC approach. And the spectral data proved that the dominant complexes are bidentate complex, and at pH6, the major Pb complex on sample G-0 surface is tridentate complex. These results are in good agreement with the CD-MUSIC fitting.
A vision for transformation of iron oxides with organic molecules in soil

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Iron (hydr)oxides are widely present in nature and nano-particles of iron minerals are distributed throughout the atmosphere, oceans, groundwater, surface waters, soils, in and/or on most living organisms. The formation of iron oxide can be improved by employing Fe(II). Furthermore, some organic molecules with hydrophilic groups on the surfaces and specific space structures, such as polymers and surfactants, can be used as electron donor and template to promote the transformation of iron oxides. Meanwhile, organic molecules, adsorbed on the crystal plane of iron oxide through the selective adsorption or special adsorption as crystal growth, influence the minerals’ morphology by the mineral’s self-assembly, oriented attachment or Ostwald ripening mechanism.

Ascorbic acid instead of Fe(II) effectively catalyzes the formation of α-Fe$_2$O$_3$, and for the first time, spherical, ellipsoidal and elongated particles of hematite have been successfully obtained by just controlling the amount of ascorbic acid. Tartaric acid as both a reducing agent and a template also control particle size and morphology of hematite. The initial pH was a crucial factor to exhibit morphology of hematite. The products were corn-like at initial pH 7 through oriented attachment, but changed to be round by ostwald ripening mechanism at high pH.

In addition, the dissolution of iron hydroxides induced by organic acids has been proposed as an important mechanism for colloid generation and removal. The inner- and outer-sphere complexes of oxalate are simultaneously present on the surface of ferrihydrite (Fh). The stabilization of Fh colloids was dominant over dissolution into dissolved Fe at a low oxalate solution concentration, driven by electrostatic repulsive forces from the unsaturated, strongly bound species. Outer-sphere complexes at a high oxalate solution concentration induced the dissolution of aggregates and colloids of Fh into dissolved Fe. Our results provided insight into the fate of iron hydroxide colloids in soils and aquatic environments.
Self-assembled composite colloids and their application to SERS detection.

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The combination of several functions within a single colloidal object has been proposed as a means to expand the potential applications of nanomaterials. A prototypical example of this class of systems is the integration of optical and magnetic properties. In particular, the incorporation of plasmonic and magnetic nanoparticles is advantageous toward the detection based on surface enhanced Raman scattering (SERS).

In this context, we present here a method to prepare colloidal hybrid assemblies that are stable in aqueous solution, while displaying interesting optical and magnetic properties, by co-encapsulation of gold nanostars and iron oxide nanocrystals within a protecting layer of poly(styrene)-block-poly-(acrylic acid) (PS-b-PAA) (Figure 1). Such a hybrid assembly combines the plasmonic properties characteristic of nanostars with the response to external magnetic fields provided by the presence of the superparamagnetic iron oxide NPs.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{(a) TEM image of individual colloid containing gold nanostars and iron oxide nanoparticles. (b) The image of hybrid clusters separated upon application of an external magnetic field. (c) SERS spectra of Malachite Green (MG) showing a strong signal enhancement upon application of the external magnetic field and particle accumulation.}
\end{figure}

We demonstrate that this hybrid colloidal system can be used as an efficient substrate for SERS detection, using common dyes as model contaminant. The co-encapsulation of iron oxide nanoparticles renders the system magnetically responsive, so that application of an external magnetic field leads to particle accumulation and limits of detection are in the nM range.

References

Organics on the Surface of Hematite Nanoparticles and the Environmental Fate of Arsenicals from ATR-FTIR, Surface Complexation Modeling and Flow Calorimetry Studies

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The environmental fate of arsenic compounds depends on their surface interactions with geosorbents that include minerals and natural organic matter (NOM). While a number of bulk batch studies reported that NOM influences arsenicals uptake, it remains unclear how different classes of organic functional groups affect their binding mechanisms. In general, molecular-level understanding of surface processes at solid/liquid interfaces demands using simple model systems and integrating spectroscopic, calorimetric, and mathematical modeling tools. In this talk, recent results on arsenicals interaction with hematite nanoparticles pre-exposed to three types of low molecular weight organics will be presented using attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR). The structure of organic surface complexes was elucidated from adsorption isotherm and pH envelope spectral data, and also modeled using the triple layer surface complexation model. Adsorption rates of arsenicals were measured and correlated with the structure of organic surface complexes. Flow calorimetric measurements were also completed to gain insight into surface charge and heats of adsorption. The significance of these results will be discussed in relation to improving modeling tools used by regulators.
How to “in situ“ probe interfaces during depollution processes?
Non-linear optic applied to molecular adsorption onto solid particles.

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Nano- and micro- particles find applications in a wide range of industrial processes. In particular, sequestrating particles are used to detoxify and to remove pollutant from liquids (water, beverage…). The ability to “in situ“ characterize the surface of particles presents significant experimental challenges as the interfaces are buried deep in the colloidal multicomponent solution. Second-Harmonic Light scattering (SHS), is a coherent nonlinear optical phenomenon, that has recently emerged as a versatile tool for characterizing the surface of colloidal nano- and micro-particles¹. To develop SHS into an effective probe of colloidal surfaces, a fundamental understanding of all phenomenons that generate second harmonic light had to be established, in particular the discrimination between the non coherent second harmonic light also called as Hyper Rayleigh Scattering (HRS) and the coherent nonlinear optical response called as (SHS).

Figure 1: Discrimination of the two SHS/HRS molecular contribution for colloidal solution: determination of adsorption isotherm and preferential orientation of the adsorbed molecules onto the particles.

In this talk, I present results on the adsorption of a chromophore dye, malachite green, onto nanometer-sized polystyrene colloidal particles in aqueous solution. The chromophore is taken as a model molecule, which mimics organic contaminant. The novelty of this study is to couple SHS/HRS measurements with a full polarization resolved experimental setup. A non linear Rayleigh Gans-Debye theory was used to describe the results and we demonstrate that the contribution of adsorbed molecule onto colloidal particles (SHS) can be distinguished -at the same time- from the contribution of equivalent molecules freely dispersed in solution (HRS), see in figure 1. I show how those measurements give a molecular description of the dye adsorption onto the nanoparticles. In particular, the adsorption isotherm and preferential orientation of the adsorbed molecules onto the particles is discussed.

References

Acknowledgement - The authors thank for Pierre-Francois Brevet’s group for fruitfull discussions.
Probing of the solid-liquid interface of adsorbing materials for food detoxification with Second Harmonic Scattering (SHS) method: example of Ochratoxin A.

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The contamination of food and beverages by mycotoxins (toxic metabolites of fungi) is one of the most significant sources of food-borne illnesses worldwide [1]. Among the toxic fungi, Aspergillus genera in particular have been shown to produce significant amounts of Ochratoxin A (OTA). This nephrotoxin is considered as particularly harmful, as it has been shown to have immunodepressive, teratogenic and carcinogenic properties [2]. Moreover, OTA can be found in a wide range of foods and regions, as Aspergillus strains grow in matrices such as cocoa and coffee beans, cereals or even fruits, such as grapes and its derivatives (wine).

Among the strategies that can be implemented to reduce the exposure to mycotoxins, food detoxification appears to be a crucial issue. For that purpose, novel adsorbing materials can be designed and synthesized to meet the health requirements in food industry. Biocompatibility, selectivity and possible implementation at industrial scale are the key qualities of a suitable system. In this study, two different materials were investigated to trap dissolved OTA in a liquid medium: Lamellar Double Hydroxydes (LDH) [3] and mesostructured silica [4].

In order to optimize the structure and functionalization of the adsorbing materials, a thorough understanding of the interfacial adsorption processes is necessary. Second Harmonic Scattering (SHS) is a novel, non-linear optical technique that was shown to be particularly powerful for local probing of interfaces in colloidal media [5]. By exploiting the intrinsic second-order optical properties of interfaces, SHS makes it possible to probe both electronic and molecular structure and dynamics at interfaces while avoiding interference from the bulk phases. The technique can probe surfaces with spectral, spatial and temporal resolution. Moreover, SHS is non-destructive and can be implemented in situ, which is a great advantage compared to usual surface analytical techniques (XPS, AES, STM, LEED...) that require preparation of the solid phase.

This study demonstrates the potential of the SHS technique to probe the solid-liquid interfaces at the molecular scale in colloidal media, in the context of food detoxification. The SHS is shown to be highly adapted to analyze the adsorption processes at the interface of materials specifically developed to trap Ochratoxin A in liquid media, making it possible to optimize the adsorbing materials structure.

References
Viruses at solid-water interfaces: assessing major interactions driving adsorption and competitive effects on adsorption in the presence of dissolved organic matter as co-adsorbate

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Waterborne viruses are responsible for a number of human diseases. As a consequence, the processes that affect the stability, transport and activity of viruses in natural and engineered water systems have received considerable research attention. One of the key processes is adsorption of the viruses to solid-water interfaces. Adsorption lowers the dissolved concentration of viruses and thus may decrease virus transport and the associated spread of infectivity. While viruses at solid-water interfaces may undergo enhanced inactivation, adsorbed viruses may also remain infective and, upon changes in solution chemistry, detach from sorbent surfaces and become remobilized. Despite the importance of adsorption, this process remained poorly understood on a fundamental level.

The objectives of the work presented in this contribution were (i) to provide a systematic assessment of the major interactions that drive virus adsorption to solid-water interfaces and (ii) to assess potential effects of dissolved organic matter (DOM) as a co-adsorbate on virus adsorption. To this end, we studied the adsorption of four negatively charged viruses (i.e., the bacteriophages MS2, fr, GA, and Qβ) as well as of negatively charged polystyrene nanospheres (as a model for viruses) onto a diverse set of sorbent surfaces under varying solution condition (pH and ionic strength). The four viruses were deliberately chosen to have capsids of comparable sizes and geometries that, however, substantially differed in their surfaces charges and polarities. We used quartz crystal microbalance with dissipation monitoring, a highly sensitive in situ surface technique, to directly quantify the initial rates, the final extents, and the reversibility of virus adsorption.

In all systems studied, virus-sorbent interactions were governed by electrostatics (which were either attractive or repulsive depending on whether the viruses and sorbent surfaces carried opposing or the same net charges) and favorable contributions from the hydrophobic effect. In comparison, van der Waals interactions and steric effects were of secondary importance. We were able to link differences in the adsorption characteristics of the four viruses to differences in their surfaces charges and polarities as assessed by modeling the distributions of ionizable and of polar and apolar amino acids on the virus capsid surfaces. Direct adsorption of all four viruses and of the nanospheres to positively charged sorbent surfaces was competitively suppressed in the presence of negatively charged DOM as a co-adsorbate. The strongly negatively charged MS2, fr, and the nanospheres experienced strong electrostatic repulsion from the DOM adlayers that formed on the positively charged sorbent surface during the co-adsorption process. As a consequence, overall adsorption of MS2, fr and the nanospheres was significantly lowered in the presence of DOM. Conversely, the less negatively charged GA and Qβ experienced net attractive interactions with the DOM adlayers due to favorable contributions from the hydrophobic effect. These favorable interactions resulted in virus adsorption to the DOM adlayers, thereby attenuating the effects of DOM as a competitive co-adsorbate on overall virus adsorption. These findings show that a detailed understanding of virus-DOM interactions is required to understand and predict the effects of DOM on virus adsorption to positively charged sorbent surfaces. The larger implications of the results of this work for the fate of waterborne viruses in natural and engineered systems will be briefly discussed.
Nature, Extent and Implications of Redox Processes in Capacitive Deionization (CDI) Water Treatment

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Whilst non-Faradaic processes, such as ion transport and capacitive storage, are at the heart of the CDI process, Faradaic reactions (i.e., redox reactions) both on the surface of and within the carbon electrodes may lead to the formation of chemical by-products and/or pH fluctuations of the produced water and the deterioration in electrode long-term stability and performance. As such, it is essential that these electrochemical processes are clearly understood if electrode stability, energy efficiency, ion removal and treated water quality are to be optimized. Importantly, it may be possible to make positive use of Faradaic effects with, for example, the production of reactive species such as hydrogen peroxide (H₂O₂) and/or free chlorine (HOCl) that may be used to induce water disinfection and/or degradation of organic contaminants.

In the studies reported here, we describe the rate and extent of Faradaic reactions in a batch-mode CDI system operating at various charging voltages (0.5-1.5 V) in the absence and presence of ion exchange membranes at the membrane surface. Of particular interest is the rate and extent of H₂O₂ generation in these systems, an example of which is shown below (from He et al [1]). In addition, we present the results of preliminary studies using a flow CDI system in which quinone compounds are used as electron shuttles with particular attention to the nature of the redox processes operating in these dynamic systems.

References
The origin of pH fluctuations in capacitive deionization

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Electrochemical systems are, amongst others, used for water treatment and desalination. Often, pH fluctuations or strong pH gradients occur in these systems. These fluctuations or gradients can cause several problems, such as the precipitation of calcium carbonate, and can result in a reduced long-term stability of electrode or membrane material. In this presentation we discuss the origin of pH fluctuations observed in electrochemical systems.

We present theory to model pH fluctuations in electrochemical systems for water treatment. We apply this theory to the case of Capacitive Deionization, a technology for water desalination employing porous carbon electrodes. Upon applying a voltage between two porous carbon electrodes, ions are adsorbed from the water and are stored in the micropores of these porous carbon electrodes, where Electrical Double Layers (EDLs) are formed [1, 2]. However, salt adsorption is not the only process that occurs; strong pH fluctuations are observed as well [3, 4]. We present a model to explain these fluctuations.

Often, in literature, pH fluctuations are ascribed to electrochemical reactions that occur during the adsorption step, when a non-zero cell voltage is applied, which can result in the production of protons or hydroxyl ions. In this work, we investigate another mechanism. Namely, as different ions have different diffusion coefficients, and consequently, different adsorption rates, pH fluctuations can already be observed. Furthermore, carboxyl and protonated groups in the micropores can adsorb or desorb protons, affecting the effluent pH of the cell.

We present a transport model for CDI, including acid-base equilibrium reactions, coupled to an EDL model, the amphoteric Donnan model, which relates salt adsorption, charge density and EDL-potential to one another, see Figure 1. We compute transport and adsorption of Na\textsuperscript{+}, Cl\textsuperscript{-}, H\textsuperscript{+}, OH\textsuperscript{-}, and consequently, the pH fluctuations and gradients. We compare our theoretical results with experimental data. Furthermore, we illustrate how our model can be applied to other electrochemical systems for water treatment.

References

Optimizing Energy Efficiency Parameters in Capacitive Deionization Systems

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We have proposed a new operational procedure to increase the energy efficiency of adsorption–desorption processes in CDI. This methodology, not published as yet to our knowledge, utilizes a concentrated brine stream as a washing solution during regeneration. We demonstrate that is possible to substantially increase round-trip energy efficiency by replacing the electrolyte during regeneration for a solution with higher conductivity. Between the deionization and regeneration stage, we implemented a constant voltage step in order not only to avoid energy efficiencies being interfered by current applied in the preceding charge or discharge stage of the process but also to allow electrolyte replacement preventing desorption of adsorbed ions. In this case, this step will necessarily last the minimum time required to empty the reactor content and to introduce the brine solution (See Fig.1). This procedure was experimentally verified in a flow cell reactor using a pair of carbon electrodes (10cm² geometric area) and NaCl solutions having concentrations between 50 and 350 mmol·L⁻¹.

In order to estimate the impact of this energy efficiency improvement in the functioning of the CDI system, the energy work required to produce 1m³ of clean solution (5 mmol·L⁻¹ of NaCl) as a function of the salt concentration at the inlet has been calculated. This has been compared to the minimum thermodynamic work results. As main conclusions, on the one hand the new operational procedure increases the energetic efficiency of the global CDI process to above 80% when charge/discharge current ratios are optimized for brackish water treatment. On the other hand, CDI operating under the selected conditions in this work could be competitive with commercially successful RO systems. We believe that this operational method might help to design the strategies for operating these systems aiming to have major impact on the practical application of this technology.

References
Modeling Ion and Water Transport in Shock Electrodialysis

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Shock Electrodialysis is a novel technology for water purification based on the formation of ion concentration polarization zones and deionization shock waves in porous media [1]. A shock-ED device consists of a weakly charged porous medium placed between two cation exchange membranes. During the operation, an overlimiting current runs through the system, causing the propagation of deionization shock waves with a sharp boundary between concentrated and depleted zones. Therefore, desalinated water and brine can be easily separated by a splitter at the outlet of the device.

Modeling the shock-ED process is a complex task, involving the description of ion and water transport in the overlimiting current region, both in the membrane and in the weakly charged porous medium. We propose a 2D model based on Nernst-Planck theory [2], where the transport of ions (both counter- and co-ions) and water is described both in the membrane and in the porous medium.

The model uses the charge density of the medium and ion diffusion coefficients as input parameters to calculate the efficiency of the process. Finally, different operating conditions are discussed for the further development of the shock ED technology.

References
Use of soft electrodes for capacitive deionization


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During the last decade a growing interest in the colloid and electrokinetic communities is emerged on a fundamental aspect of electrical double layers, namely, their capacitance and its dependence on the potential and the ionic strength [1]. Such interest is associated to the possibility of either obtaining energy or cleaning (desalinating) solutions based on the increased capacitance when the ionic strength is raised. In this work, we will focus on the second phenomenon, CDI or capacitive deionization [2], where the ions dissolved in a salty solution are partially removed under the application of an electric potential when the solution fills the space between porous electrodes. Most previous works are based on the use of carbon electrodes for the electrodes either bare or in contact with ionic exchange membranes (MCDI). In this contribution we propose a new approach inspired in the electrokinetics of soft particles: a layer of polyelectrolyte (cationic on one electrode, anionic on the opposite one) coats the carbon electrodes, converting them in a sort of “soft” electrode pair [3]. The polyelectrolyte coatings play a similar role to the ionic exchange membranes, with the key advantage of cost, ease of preparation and, presumably, durability. We present a theoretical model and a set of experiments showing how soft electrodes perform in capacitive deionization in comparison with bare ones and with MCDI.

Figure 1: Left: Schematic representation of two carbon electrodes coated by a cationic and an anionic polyelectrolyte immersed in an electrolyte solution and externally connected through a power source. Right: Data for effluent salt conductivity and current as a function of time in CDI during adsorption and desorption. The feed salt concentration is 20 mM and the voltage cell, 0.9 V.

References

Acknowledgement- The authors thank MINECO (Spain) and FEDER Funds (EU) for financial support through project FIS2013-47666-C3-1-R and S. Ahualli thanks to “Vicerrectorado de Investigación y Transferencia, Universidad de Granada” for her postdoctoral grant.
Poster presentations
Adsorption of triclosan on recycled adsorbent materials

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Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) is a common synthetic antimicrobial agent that has been incorporated into more than 700 different industrial and personal care products. The content was found to be in the range of 0.1 - 0.3%. The widespread use of triclosan provides a number of pathways to enter the environment. Moreover, upon exposure to sunlight or UV light, environmental triclosan can be transformed into more toxic compounds such as chlorinated dioxins. In addition, reports suggest that the incineration of textile products containing triclosan may result in the formation of dioxin-like substances. The primary disposal route for many of these ingredients is the municipal wastewater collection and treatment system and finally the aquatic environment. Due to the uncertainty in estimating the environmental release via this pathway, no predicted environmental concentration (PEC) in surface waters has been derived.

Activated carbons are traditional and effective adsorbents for the treatment of industrial wastewater. The advantages of coal based carbons can be seen in their ability to remove toxic organic compounds from industrial and municipal wastewater and potable water as well. That is why it is crucial to study the adsorption of triclosan as a model system by various sorbents. The adsorption of triclosan as model system is studied to qualify activated carbon sorbents recycled from gas masks (civilian gas mask GP5). The triclosan equilibrium concentration is measured spectrophotometrically, the morphology of the activated carbon is characterized by scanning electron microscopy, the amount of the adsorbed triclosan on the activated carbon is quantified by a mass balance method. Experimental isotherms are fitted by Langmuir, Freundlich and Sips isotherms models. It is obtained that the contact time is a crucial sorption parameter that provides information on the optimum adsorption efficiency. It is shown that the maximum efficiency of GP5 (88%) is obtained after 10 days of adsorption at a maximal concentration of triclosan and carbon loading 1mg/l. No significant adsorption efficiency differences are measured after 5 and 10 days of adsorption. It is shown that the non-linear Sips isotherm, a combined Freundlich–Langmuir model, provides suitable fitting results. Obtained remarkable adsorption capacity of activated carbon (GP5) towards triclosan adsorption (~85 mg/g) making it viable solution for the wastewater treatment.
Use of polymer/surfactant mixtures for the encapsulation of active ingredients

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Polyelectrolyte capsules produced by polyionic assembly (Layer by layer technique) are the most popular for the encapsulation of sensitive reagents which use the oppositely charged polyelectrolytes (polycations and polyanions) to form a multi-layer membranes. However, this method has several disadvantages: a multistage process consisting in applying polyelectrolyte layers with multiple rinsing procedure after each application, additional dissolution of core for the formation of a hollow capsule and subsequent loading of the active ingredients.

Thus, there arises the problem of modifying an existing method of encapsulation. The using of polymers combined with surfactants, frequently used as a wall material in microcapsules formation processes, are promising approach of the microencapsulation. The polymer/surfactant complexes can change the adsorption layer around the oil droplets which affect on thus emulsion stability, and hence the possibility of film formation.

The main objective of this work is to study the encapsulation of vitamine E (alpha-tocopherol) by layer-by-layer multilayer method depending of the different wall compositions. As wall materials the mixture of anionic polyelectrolyte PSS with cationic surfactant CTAB as a first layer, then layer- by layer assembly oppositely charged chitosan, then PSS were used. The optimal conditions (conditions of emulsification, layering, encapsulation and etc) were determined. Stability of emulsions and microcapsules (charge and size distribution) were studied by Dynamic light scattering. The size distribution of initial emulsions, intermediate and final microcapsules was measured directly after emulsion formation by using a Zetasizer (Malvern), and repeated over 10 days. The results showed good stability of them and the sizes were around 1-1.5micron with PDI=0.3. The sizes of capsules were confirmed by Cryo-SEM and confocal microscope. Zeta-potential of the investigated capsules changed from -45 mV to +40mV in each layering. The zeta potential value of final capsules are -40mV. Such difference (80-85mV) shows good stability effects.
Adsorption of Tetracycline by geomaterial matrix: Adsorption equilibrium and kinetics

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Abstract

The use of antibiotics in human and veterinary medicine has grown considerably in recent years, as feed supplement to enhance animal growth. This large number of use has allowed detection of residues in water and wastewater. This can lead to new strains of bacteria resistant to these antibiotics and incurable diseases of livestock and humans. Tetracyclines have the potential to reach soil and aquatic environment. This work aims to develop a new composite material called geomaterial (GM). This composite is based on treated bentonite of Maghnia (ATMa) (80%), activated carbon, cement and polyvinyl alcohol (PVA) for containment of hazardous waste in landfills.

The removal of tetracycline (Tc) from the aqueous solution was tested on GM and its mineral constituents. The Tc adsorption isotherms on studied adsorbents showed that removal was better on activated carbon ($Q_a = 157.24$ mg.g$^{-1}$) and GM ($Q_a = 75.5$ mg.g$^{-1}$) compared to ATMa. Furthermore, adsorption capacity is pH-dependant, the higher adsorbed amount of Tc is obtained at pH 2.
Measuring the uptake of Cobalt/Iron/Mg ions by inorganic/organic resources in carbon xerogel as a CDI electrode material

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Carbon xerogel have been considered as a promising candidate in capacitive deionization systems (CDI). The assemblage of some compounds with pseudocapacitance and carbon nanoporous materials can improve its capacitance performance. One of the most important concepts in the infiltration of secondary compound through a carbon scaffold is to evaluate the amount of confined material. Because the effective particles that will increase the capacitance of the final electrode are the portion which have placed inside the scaffold pores.

Three carbon xerogel samples have been synthesized in three different pH values following to the path suggested by Hwang et. al (2004). In two cases the physical activation was carried out at 900°C in a continuous flow of CO₂ for 4 hours. The impregnation of iron/cobalt was carried out on final heat treated carbon xerogel by dissolving the nitrate resources of Iron and cobalt in deionized water and immersing a piece of carbon xerogel in the solution overnight. The infiltrated gels removed from the solution and loaded into an autoclave to remove water and decompose the metal nitrate to oxide under vacuum at 400 °C. All surfaces of the samples were scratched by abrasive paper (1000 girt) to remove the oxides remained on the surfaces of xerogel.

The surface area of synthesized carbon xerogel have been studied by BET method. The trend of pore size and volume reduction of sample on increasing the initial pH is in agreement with previous studies. As a consequence of the activation process, a larger specific surface but a constant pore diameter was observed. The different substances used for infiltration experiments in the xerogel, with concentrations of their solutions are reported in Table 1. The ideal uptake is calculated by multiplying the solution concentration by the gel specific volume, whereas the experimental one was determined by ICP analysis of the infiltrated samples. ‘Scratched’ and ‘non-scratched’ specifications refer to the surface treatment of xerogel after infiltration. By comparison of uptake values for scratched and non-scratched iron containing samples, it can be concluded that about half of the expected (ideal) Fe content was not confined but have just covered the gel surface as bulk iron.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Surface</th>
<th>Conc. (mmol/g gel)</th>
<th>solution conc. (M)</th>
<th>Gel Total Vol (cc/g)</th>
<th>Calculated uptake (mmol/g gel)</th>
<th>Exp./Calc. uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(BU)₂</td>
<td>Scratched</td>
<td>0.91</td>
<td>3.00</td>
<td>1.09</td>
<td>3.27</td>
<td>27.89</td>
</tr>
<tr>
<td>Mg(BU)₂</td>
<td>Scratched</td>
<td>0.98</td>
<td>1.00</td>
<td>1.09</td>
<td>1.09</td>
<td>90.09</td>
</tr>
<tr>
<td>Fe(NO₃)₃</td>
<td>non-Scratched</td>
<td>0.71</td>
<td>0.99</td>
<td>1.20</td>
<td>1.19</td>
<td>59.75</td>
</tr>
<tr>
<td>Fe(NO₃)₃</td>
<td>Scratch</td>
<td>0.33</td>
<td>0.99</td>
<td>1.20</td>
<td>1.19</td>
<td>27.39</td>
</tr>
<tr>
<td>Co(NO₃)₂</td>
<td>non-Scratched</td>
<td>1.11</td>
<td>0.99</td>
<td>1.20</td>
<td>1.19</td>
<td>93.28</td>
</tr>
</tbody>
</table>

Table 1. Results of ICP analysis on different carbon xerogel.

The lower value of truly confined iron and cobalt with respect to magnesium in the gel is related to the different character of the infiltration solutions. Fe and Co were contained in water solution but magnesium dibutyl was in an organic solution. Solution uptake is due to capillary pressure inside the scaffold pores which is a function of wettability. RF carbon aerogel/xerogel are known to be hydrophobic compounds, so that the capillary force and uptake capability of carbon scaffolds in water media is less than in organic solutions. The value of infiltrated Mg compound cannot be increased by increasing the concentration of the starting solution, because the viscosity also increases with concentration so as to affect the uptake value.

In conclusion, it have been observed that the nature of the resources solution plays the main role in the amount of ion uptake inside the carbon scaffold. Moreover a larger portion of the selected ion will stay on the surface of the scaffold which will not permanently improve the capacitance behavior of the electrode.
Approaches to enhancing the performance of RF carbon gels dried in ambient pressure for CDI electrodes

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RF carbon gels, benefited from wide range of specific surface area and simple preparation procedure, are known as the most important electrode materials for capacitive deionization. In the light of extensive application of this material, it suffers from large amount of shrinkage during preparation, which can eventually reduce its performance in CDI method. In the carbon gel product process, the most common way for extracting liquid from wet-gel, is Subcritical drying in ambient pressure. The produced porous material is called Carbon xerogel. Producing carbon xerogel is usually accompanied by huge amount of shrinkage. This problem can be addressed by:

- trying other drying methods such as supercritical and freeze drying, which produces aerogels and cryogels, respectively.
- Manipulation of the effective synthesis parameters.
- Adding some additives to the structure of CDI electrodes.

Some disadvantages such as limitation in sample size, the special required equipment and complex preparation procedure are caused supercritical and freeze drying methods (the first mentioned proposed approach) less desirable for large scale RF carbon gels production.

Table 1 presents a review on papers published about the preparation of carbon xerogel with different values of effective parameters. Herein, the final shrinkage (%), specific surface area (m²/g) and specific capacitance (F/g) of the product are selected as the objective parameters.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R/F (Molar ratio)</th>
<th>R/C (Molar ratio)</th>
<th>Mass fraction of reactants in liquid</th>
<th>Exchange the water with acetone</th>
<th>Shrinkage before pyrolysis</th>
<th>Pyrolysis temperature</th>
<th>Pyrolysis duration</th>
<th>Shrinkage after pyrolysis</th>
<th>BET surface area (m²/g)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Saliger et al., 1997) Sodium Carbonate</td>
<td>0.5</td>
<td>1000</td>
<td>30%</td>
<td>yes</td>
<td>5%</td>
<td>1050°C</td>
<td>22.5%</td>
<td>147</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pröbstle, Wiener, &amp; Fricke, 2003) Sodium Carbonate</td>
<td>0.5</td>
<td>1500</td>
<td>30%</td>
<td>yes</td>
<td>800°C</td>
<td>649</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Lee et al., 2010) Sodium Carbonate</td>
<td>0.5</td>
<td>500</td>
<td>40%</td>
<td>yes</td>
<td>Negligible</td>
<td>800°C</td>
<td>2 hr</td>
<td>706</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>(Nguyen, Yang, &amp; Chung, 2015) Glacial Acetic Acid</td>
<td>yes</td>
<td>850°C</td>
<td>3 hr</td>
<td>661</td>
<td>218</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Li, Yang, &amp; Zhang, 2015) Cetyltrimethyl Ammonium</td>
<td>0.5</td>
<td>125</td>
<td>no</td>
<td>900°C</td>
<td>3 hr</td>
<td>2477</td>
<td>201</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Some previous studies about preparation of carbon xerogel with different amount of effective parameters

Some previous literatures about assessing effects of additional compounds on the carbon xerogel structure are condensed in Table 2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R/F (Molar ratio)</th>
<th>R/C (Molar ratio)</th>
<th>Mass fraction of reactants in liquid</th>
<th>Exchange the water with acetone</th>
<th>Shrinkage before pyrolysis</th>
<th>Pyrolysis temperature</th>
<th>Pyrolysis duration</th>
<th>Shrinkage after pyrolysis</th>
<th>BET surface area (m²/g)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Glora, Fricke, &amp; Petrovic, 2001) Using carbon and Al₂O₃ fiber reinforced</td>
<td>0.5</td>
<td>1500</td>
<td>30%</td>
<td>yes</td>
<td>0%</td>
<td>1050°C</td>
<td>4 hr</td>
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<tr>
<td>(Wang et al., 2001) Using carbon cloth reinforced</td>
<td>0.5</td>
<td>1500</td>
<td>30%</td>
<td>no</td>
<td>0%</td>
<td>1000°C</td>
<td>2.3 hr</td>
<td>396</td>
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<tr>
<td>(Pröbstle et al., 2003) Using carbon fiber reinforced</td>
<td>0.5</td>
<td>1500</td>
<td>60%</td>
<td>yes</td>
<td>800°C</td>
<td>566</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Landon, Gao, Kulangoorid, Neathery, &amp; Liu, 2012) Using Flexible conductive carbon cloth substrate</td>
<td>0.5</td>
<td>1500</td>
<td>50%</td>
<td>yes</td>
<td>1000°C</td>
<td>2 hr</td>
<td>239.1</td>
<td>28.6</td>
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<td></td>
</tr>
<tr>
<td>(Huang, Wang, Zhang, &amp; Xing, 2015) Using ammonia as catalyst and The MoS2/carbon aerogel hybrid</td>
<td>no</td>
<td>650°C</td>
<td>15 hr</td>
<td>918</td>
<td>260</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(Kumar et al., 2016) Using Resorcinol, Formaldehyde, tetraethyl orthosilicate and 3-aminopropyl tri-ethoxysilane</td>
<td>yes</td>
<td>900°C</td>
<td>1 hr</td>
<td>2600</td>
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</table>

Table 2: Some previous studies about effects of additional compounds on the carbon xerogel structure

In summary, carbon xerogel composite can be nominated as an ideal electrode for CDI desalination method aimed at limiting the total shrinkage of the synthesized carbon xerogel. Furthermore, the use of fibers in the proposed composites will improve electrode conductivity and in some cases create a pseudocapacitance in the final electrode.
TCE removal Properties of Synthesized Modified Nano-Clay Minerals with Zn ions

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Abstract
The occurrence of Non-degradable organic compounds and xenobiotic chemicals in water environment has great concerns to the public because of their polar properties and toxicity. Trichloroethylene(TCE) is one of the widely used as solvents in the chemical industry, and TCE is now a contaminant of soil, surface water and groundwater. Recently, studies on new treatment technologies showed that advanced oxidation processes using photocatalyst is one of the most appropriate treatment to remove these polar and toxic compounds from water. The object of this study was to remove of TCE in water using synthesis of modified nano-clay minerals with Zn ions. The nano-clay mineral used in this experiment is Laponite RD, which is an inorganic protective powder of disilicate structure. As a result of experimenting the application of TCE decomposition by synthesizing a modified nano-clay mineral with Zn ion in order to review the possibility of replacing an expensive TiO₂ photo catalyst which is used in purifying underground water. We confirmed the effects of modified nano-clay minerals with Zn ion for decomposition of Trichloroethylene compounds.

References
Chromium accumulation in harbor sediments: estimations of anthropogenic enrichment, bioavailability and potential adverse biological effects.

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Significant dredging activity is constantly required to enlarge, deepen and maintain harbor access and activities. However, the management of dredged marine sediment is an issue, particularly when the concentrations of the contaminants - such as metals - prevent the sea or land disposal of the sediments, due to possible re-mobilisation of toxic elements. The accumulation of metals in sediments is based upon a range of key factors: natural background levels, sediment mineralogical composition, anthropogenic activities and inputs.

The knowledge of the total concentrations of metals is useful to calculate various contamination indexes, but are not sufficient to predict the real potential adverse effect on the environment: the metals toxicity depends on other parameters such as mobility and bioavailability. Indeed, adsorbed metals are potentially available from the sediments as they may be dissolved due to changes in salinity, pH, redox conditions, organic chelators occurrence... Many studies focus on an evaluation of anthropogenic inputs others on the potential bioavailability of elements; for a comprehensive environmental risk assessment, both approaches are essential in order to fully characterize the sediments.

The results presented in this study focus on the chromium element detected in sediments sampled from 13 harbors across the English Channel. The mineralogical speciation of Cr and its potential mobilization (or lability) and bioavailability was studied thanks to a sequential extraction procedure. The total concentrations of Cr, determined after acid microwave assisted mineralisation, were used, on the one hand, to calculate the enrichment factor (EF) that should help to visualize atypical enrichment which may be anthropogenic. On the other hand, they allow the calculation of Adverse Effect Index (AEI), to estimate the possible adverse biological effects of Cr in the studied sediments. We then investigate the possible relationships between the enrichment, mobility and possible biological effects.

Acknowledgement – The authors thank the financial support of the European Regional Development Fund (ERDF), Interreg IVA and Regional Council of Basse-Normandie. ...
Kinetic and thermodynamic study of boron removal by ionic or boron selective resins in batch reactors

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Boron is an element which is considered as a nutrient for living organisms, mainly for plants where it is involved in cell wall structure as complexed with sugars. But its excess can cause some health or ecotoxicological problems. The main bad influences are on the development of plants, humans and animals such as nausea, diarrhoea, dermatitis, lethargy and defoliation, decay and fall unripe fruits. The World Health Organisation (WHO) has recommended a guideline of 0.5 mg boron L⁻¹ in drinking water and a maximum limit of 0.3 mg boron L⁻¹ in fresh water used for irrigation¹. Due to the shortage of fresh water sources, desalination of seawater, where the boron concentration is quite high (5 mg L⁻¹), has been becoming an alternative fresh water supply. Boron removal from seawater or contaminated fresh water would be a prerequisite to produce water having the standard WHO guideline levels. Several separation technologies are often applied during desalting water such as adsorption, precipitation, coagulation, reverse osmosis, solvent extraction and ion exchange. Among them, the most common method used is boron adsorption by either anionic or specific resins. The aim of our work was to compare the kinetic and thermodynamic behaviour of two specific boron resins, Amberlite IRA 743 and Diaion CRB 03, and two anionic resins, Ambersep 900-OH and Amberlite IRA 402 Cl, with respect to their retention capacity.

The set of experiments was performed to study the mechanisms of boron surface exchange vs. time and at equilibrium depending on physicochemical parameters such as contact time, pH, initial concentration, using batch reactors with the two types of resins, at room temperature.

At initial pH 8, high percentage of boron adsorption was obtained within a half-hour, which showed a fast reaction between solid and liquid interface for the three resins, Amberlite IRA 743 (98 %), Diaion CRB 03 (98 %), Ambersep 900-OH (96 %). On the other hand, the Amberlite IRA 402 Cl resin showed a slow rate and low boron sorption with only 10 % removal even after 24 h adsorption. Experimental results showed that equilibrium was reached after 2 h reaction time for the four resins. The pseudo second-order kinetic model was used to estimate kinetic parameters. Comparison between experimental and fitted parameters showed that the kinetic sorption processes are well described for all the resins.

At equilibrium, we showed that the boron sorption on Amberlite IRA 743 and Diaion CRB 03 did not depend on pH from 6 to 12. This behaviour can be explained by formation of surface complexes between boron and the polyhydroxy functional groups, such as the N-methyl-D-glucamin², present at the resin surface, either for neutral or for alkaline pH values. On the other hand, the anionic resins, Ambersep 900-OH and Amberlite IRA 402 Cl, exhibited a highest sorption capacity at pH 8 and 10, respectively. Ionic exchange is controlled by competition with OH⁻ ions at high pH for both resins and mainly by competition with Cl⁻ ions at low pH for the Amberlite IRA 402Cl resin.

Isotherm experiments for each resin were performed at initial pH 8. The maximum boron sorption capacities of the resins were estimated to reach 1.07 mmol g⁻¹ (Amberlite IRA 743), 0.87 mmol g⁻¹ (Diaion CRB 03), 0.38 mmol g⁻¹ (Ambersep 900-OH) and 0.24 mmol g⁻¹ (Amberlite IRA 402 Cl). Different sorption models were used to fit experimental isotherms. In the range of boron concentrations studied, (i) the Langmuir-type relationship was applied to the Diaion CRB 03 and Ambersep 900-OH resins for fitting the maximum sorption capacity and the Langmuir-type coefficient; (ii) the BET-type relationship was used for describing the boron behaviour in the presence of the Amberlite IRA 743 resin and for estimating the boron sorption capacity and the BET-type coefficient; and (iii) the Henry-type model was used for fitting boron sorption behaviour in the case of the Amberlite IRA 402 Cl.

From all the obtained results, we will compare all the resins and discuss their efficiency with respect to their potential impact on the environment for removing boron at a better cost.

References

Acknowledgement - Hien Thi Thu Nguyen was supported by a grant from Vietnam International Education Development (VIED) and the Vietnam-France University, University of Science and Technology of Hanoi (USTH).
Combining silver nanoparticles and gold electrode for the detection of nitrate at low level in seawater

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Since 40 years, many studies have been dealing on the nitrogen cycling in the environment due to its use as fertilizer in agriculture. Indeed, they are a well-known contaminant of ground and stream water. Nitrate is an important environmental and human health analyte1,2. At high concentrations in aquatic systems, nitrate as phosphate plays an important role by changing the biological equilibrium mainly by contributing to an excessive growth of phytoplankton leading to eutrophication in coastal areas for nitrates. The concentration range of nitrate in inland waters is between 10 and 1600 µM. The European water drinking guideline is fixed to 50 mg L−1 (800 µM).

In seawater, the nitrogen cycling is one of the most complex cycle of the nutrients. Nitrogen limits the primary biologic production and influences the other biogeochemical cycles (carbon, phosphorus...). Its cycle plays an important role in the oxygen minimum zones of the oceans, at rather low concentration (nanomolar concentration). In the specific area of oceanography, there is a growing demand for the oceans observations and to better understand biogeochemical cycles and mixing of water masses, the development of simple, low-power, sensitive, selective and stable analytical in-situ sensors appears as a necessity.

The aim of this study is to develop an electrochemical sensor in order to measure nitrates at very low concentration (nanomolar) in seawater (pH ca 6). We present here an original way for the functionalization of a gold electrode (E Au ) using an organometallic silver precursor. Well dispersed AgNPs are obtained with small size and narrow distribution. The advantage of this resulting nanostructured surface combines the advantages of the electrochemical properties of the gold electrode and the presence of silver nanoparticles, AgNPs (Figure 1). This has been obtained in our previous work obtained with electrodeposited Ag nanoparticles (AgNPs) in aqueous medium using a silver salt (AgNO3).

The results obtained for different synthetic nitrate solutions using AgNPs modified-gold electrode will be discussed.

References

Acknowledgement – This work is partially supported by a grant from the Foundation RTRA “Sciences et Technologies pour l’Aéronautique et l’Espace” of Toulouse
Electrochemical pre-treatment on nickel electrode prior to a biological treatment for tetracycline removal

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Biodegradability improvement of tetracycline-containing solutions after an electrochemical pre-treatment was examined. Cyclic voltammetry with a nickel electrode revealed a significant electrochemical activity of tetracycline, in both oxidation and reduction. Electrochemical treatment was therefore performed in a home-made flow cell using a nickel-modified graphite felt electrode as the working electrode. Optimal conditions, namely 100 mg L\(^{-1}\) initial tetracycline, above 0.45 V potential, and between 1 and 6 ml min\(^{-1}\) flow rate, led to a more than 99% conversion yield of tetracycline in oxidation in alkaline conditions, after only a single pass through the percolation cell. However, total organic carbon (TOC) analyses revealed a low mineralization level, i.e., always below 31%, underscoring the importance of a combined electrochemical and biological treatment. This was confirmed by the favorable trends of the COD/TOC ratio, decreasing from 2.7 to 1.9, and the average oxidation state, increasing from 0.044 to 1.15, before and after oxidation pre-treatment at 0.7 V and 3 ml min\(^{-1}\) flow rate. Electrolyzed solutions appeared biodegradable, since BOD\(_5\)/COD increased from 0 to 0.46 for untreated and pretreated TC at 0.7 V/SCE. Biological treatment showed only biosorption for non-pretreated tetracycline, while after 11.5 days of culture, the mineralization of solutions electrolyzed in oxidation was 54%, leading to a 69% overall TOC decrease during the combined process.
Screening of emerging chlorophenols at ultra-trace levels in environmental waters by solid phase extraction combined with ultra-high performance liquid chromatography

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Drinking water chlorination plays an important role in preventing pathogen contamination that causes waterborne diseases. However, the negative health effects which have been associated with the consequently formed disinfection by-products (DBPs) from the reaction between chlorine and organic matters in water have driven much attention in recent years. More than 600 DBPs have been reported in the literature. Among them, chlorophenols (CPs) formed during the disinfection treatment of water with chlorine, are considered as highly toxic and carcinogenic. The majority of CPs found in water are: monochlorophenol, dichlorophenol, trichlorophenol and pentachlorophenol. Moreover, few data exist about the content of emerging CPs which are present in water samples at very low concentrations (in the order of ng L\textsuperscript{-1}). Thus, knowledge on the occurrence of these compounds in water is important for sanitary and future regulatory purposes. In this study, ultra-high performance liquid chromatography (UHPLC) coupled to a photodiode array detector (PDA) was used for the development of an analytical method capable of simultaneous identification and quantification of four CPs in water samples. A solid phase extraction method (SPE) was optimized for the extraction and pre-concentration of target analytes. The chlorophenols were separated by an Acquity BEH C18 (100 x 2.1 mm, 1.7 μm) column with a mobile phase of acetonitrile/ultrapure water/formic acid. The flow rate of the mobile phase was 0.4 mL min\textsuperscript{-1}. The optimized SPE-UHPLC/PDA technique was evaluated in terms of robustness, considering the enrichment factor for all of the studied chlorophenols. Linear calibration was obtained with correlation coefficients $r^2 \geq 0.998$. The obtained extraction recoveries were higher than 99%. The pre-concentration factor was 2.500 for all analytes. Under optimized conditions, the detection limits of the overall SPE-UHPLC/PDA method were in the ng L\textsuperscript{-1} levels. The excellent performance of the developed method, as well as the short analysis time makes it a promising analytical tool for the screening of chlorophenols in environmental water samples.
Development of predictive models for the formation of trihalomethanes and haloacetic acids during chlorination of water

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Disinfection is the most important process in the treatment of drinking water supply and is the final barrier against pathogenic bacteria and viruses before its distribution to consumers. However, water disinfection with chlorine and chloramines results in the formation of disinfection by-products (DBPs), which are of potential human health concern. In recent decades, research efforts have focused to a better understanding of the formation kinetics of these compounds and on the development of mathematical models capable to predict and control their individual formation. Different modeling approaches have been used to relate water quality (TOC, SUVA, bromine content ...) and operating parameters (pH, temperature, chlorine dose, contact time,...) with DBPs concentration in water. Some researchers have used empirical equations and others semi-empirical models based on assumptions of reaction mechanisms, which theoretically could be extended to a larger number of systems than empirical models, more dependent to the reactor design and experimental conditions. The aim of this study was to develop and validate at laboratory scale, an experimental methodology allowing the study of simultaneously formation of two classes of DBPs during the chlorination process. The DBPs studied here were the trihalomethanes (THMs) and haloacetic acids (HAAs). Moreover, a semi mechanistic model able to predict their generation in raw waters was also developed. Chlorination tests were carried out at laboratory scale, in a reactor of 40 liters. For the experimental kinetic study 12 individual reactors of 2L were then filled with the chlorinated water, each one is a kinetic point. All tests were done in the dark, in a wide range of experimental conditions (pH, temperature and chlorine initial dose), using a groundwater sample collected from a well. THMs and HAAs concentrations were measured using a head space-GC/MS method. For the used raw water characterization different parameters were determined (dissolved organic carbon, and nitrites, nitrates, ammonium, and bromide content). Experimental results show similar time profiles for the THMs and HAAs species. Two distinct formation mechanisms were observed for these compounds: one faster and then it decreased for all DBPs considered species until a level of concentration. Moreover, it was observed that THMs species were more predominant than total HAAs. Comparison of the experimental and simulated results confirms the model ability to predict THMs and HAAs formation. Moreover, kinetic constants, activation energies and reaction rate order for the formation DBPs species were subsequently determined. A semi-empiric model capable to simulate the THMs and HAAs formation during the chlorination was developed in this study. Although the good correlation between the simulated and experimental data, further investigation is necessary to verify the performance of the model in a wider range of operating conditions.
The presence of heavy metals in industrial wastewaters and natural waters is a major problem in different areas of the world due to their high toxicity, which encourages the development of separation systems for the treatment of polluted waters. Polymer inclusion membranes (PIMs) are expected to provide efficient and cost-effective for the treatment of polluted waters [1]. The components of most of the PIMs are: a) a base polymer, b) an extractant or carrier and c) a plasticizer. The role of the base polymer is to provide the membrane with mechanical strength, but it also must entrap the active component (carrier) and to minimize any loss of the carrier on the surrounding solutions, while the plasticizer is mainly used to improve the flexibility of PIMs. However, the use as carriers of room temperature ionic liquids (RTILs), which also have plasticizing abilities, has provided flexible membranes without the need of adding any other component [2].

In this work, a comparison of chemical, elastic, electric and diffusive transport differences between two PIMs fabricated with the same polymer, cellulose triacetate (CTA), and content of RTIL (Aliquat 336, a mixture of quaternary ammonium chlorides), but different amount of the plasticizer (2-nitrophenyl octyl ether, NPOE) was performed to determine the effect of this latter component in the membrane behavior.

The two PIMs studied were prepared by dissolving CTA in the appropriate solvent as it was extensively explained in [3]. Membrane composition was 70 % CTA plus 30 % Aliquat 336 (sample CTA/Aliquat) and 50 % CTA plus 30 % AliquatCl and 20 % of NPOE (sample CTA/Aliquat/NPOE). Chemical characterization of both membranes was carried out by XPS and IR, while information on mechanical and electrical parameters was obtained from elastic curves and impedance plots, respectively, using dry membrane samples. Moreover, membrane potential measurements using solutions of a model electrolyte (NaCl) were also performed for analysis of ions diffusive transport.

The obtained results do not show significant chemical surface differences between both membranes but, as expected, the addition of NPOE improves its elastic properties. In addition, the use of plasticizer seems to significantly reduce the electrical resistance of the PIM, and it also slightly affects the diffusive transport of positive ions (Na+) across the membrane.

References


Acknowledgements - The financial support of Research Project CTM2013-48967-C2-2-P, Research group FQM 258 (Junta de Andalucía) and the doctoral grant ref. BES-2014-068316 (R.V.) are acknowledged.
Electrochemical characterization of a regenerated cellulose membrane modified by Janus Ag-nanoparticles inclusion

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Cellulose, the most abundant natural polymer, is a high hydrophilic material commonly used for membrane manufacture. The hydrophilicity is an important characteristic of membranes material since it reduces membrane fouling, which is a significant problem in the industrial use of ultrafiltration (UF) and nanofiltration (NF) membranes. However, the elastic characteristic of cellulose-based membranes (such as regenerated cellulose or RC) may reduce their application to UF and NF processes due to membrane compaction under the range of pressure used in such processes [1]. The inclusion of solid nanoparticles in the membrane structure may be a way to improve the mechanical behaviour of cellulosic membranes, and in the case of silver nanoparticles (AgNPs) they can also enhance their oxidative character. Moreover, spherical AgNPs with different chemical character on each hemisphere (or Janus AgNPs) might also affect other important characteristic membrane parameter for the transport of solutes (even ions or charged species) such as the effective fixed charge in the membrane (Xf), diffusive permeability (Ps) and diffusion coefficients (Di).

This work presents the electrochemical characterization of a highly swollen regenerated cellulose membrane modified with Janus AgNPs (RC-6/J-AgNPs membrane) by measuring salt diffusion permeability (Ps) at a wide range of NaCl concentrations (from 10⁻³ M to 0.2 M). Elastic (strength-elongation curves) and in impedance spectroscopy (IS) measurements with both RC-6 and RC-6/J-AgNPs membranes were also performed to get a more complete picture of the changes associated to the Janus-Ag nanoparticles inclusion. Janus Ag-NPs were prepared by following the procedure described in ref [2]. Fig. 1 shows SEM micrographs of the Janus Ag-NPs (a), and the surface of the RC-6/J-AgNPs membrane (b).

![Fig. 1: SEM micrographs of: Janus Ag-NPs (a), the surface of the RC-6/J-Ag-NPs membrane (b).](image)

Impedance Spectroscopy (IS) diagrams show significant differences when plots obtained for dry RC-6 and RC-6/J-Ag-NPs samples are compared, but only small differences seem to exist in the case of wet samples (after 24 h in a 10⁻³ M NaCl solution) [3]. On the other hands, the analysis of the Ps-C curves [3-4] also show differences in both salt diffusion coefficient and effective fixed charge (values increase of around 30 % and 17 %, respectively) for the transport of NaCl across the RC-6/J-Ag-NPs membrane with respect to values obtained for the RC-6 support membrane.

References

Acknowledgement - We thank Junta de Andalucía for financial support (Research group FQM 258).
Different techniques for fouling characterization of porous membranes: Application to a ceramic-BSA fouled membrane

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Porous structures and membranes are employed for filtration of macromolecules solutions or colloidal particles commonly used in food and pharmaceutical industries. Depending on the solution-membrane characteristics, different filtration processes can be considered: microfiltration (MF), ultrafiltration (UF) or nanofiltration (NF). For these two latter processes, membrane fouling or the adsorption/deposition of particles on the membrane surface (including pore walls) is a great problem, since it usually causes a significant reduction in the solution flow ($J_v$) at a given pressure difference ($J_v = L_p DP$) and, consequently, a loss in the effectiveness of the process. Reduction in the hydrodynamic permeability ($L_p$) as well as changes in the streaming/zeta potential values use to be determined for membrane fouling information. On the other hand, nanoporous membranes are lately being used for drug delivery application in flow processes associated to a concentration difference at both membrane sides ($J_s = P_s DC$). Among other systems, devices based in thin ($D_x < 100$ mm) nanoporous alumina membranes (NPAMs) with planar geometry obtained by the two-step anodization method [1] are lately being employed for such application [2-3]. Although the adsorption/deposition of macromolecules associated to diffusion could be lower than in filtration processes, it might also affect the diffusive flux, but due to the fragility of NPAMs different types of measurements able to provide information on membrane modification (without involving pressure difference) are necessary.

This work reports changes in a commercial ceramic membrane as a result of both protein (bovine serum albumin or BSA) filtration and “static” fouling associated to its diffusive transport. A planar, flexible and symmetric composite ceramic membrane from Degussa, Germany [4] was used for effects comparison. Reduction in the hydrodynamic permeability (50 % for tangential cell and 65 % for dead-end cell) and in the z-potentials measured at different pHs ($C = 10^{-3}$ M NaCl), clearly shows the presence of BSA on the membrane pore wall, while XPS analysis was used for external surface information. Moreover, membrane fouling associated to BSA/membrane diffusive contact was analyzed by comparing membrane potentials ($DF_{mbr}$) measured at different NaCl concentrations also for both clean and statically BSA-fouled membranes.

References

Acknowledgements – The authors thank to Junta de Andalucía for the financial support of Research Group FQM 258.
Study of the dyes degradation in wastewater from textile industry

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The Advanced Oxidation Process (AOP) are promising environmentally friendly technologies for the treatment of wastewater containing organic pollutants. The objective of our work is to study the possibility of destroying the dye Methyl Orange by some POA then compare the efficiencies of the processes used (Fenton, photo-Fenton and electro-Fenton). Our study therefore focused on the degradation of this toxic dye. The comparative study of Fenton, photo-Fenton and electro-Fenton processes revealed that the electro-Fenton is the best method for oxidizing the dye. The dye of the degradation kinetics by the electro-Fenton process is very fast where the degradation rate reached 90.87% after 5 minutes. The degradation of organic matter was monitored by UV / Visible spectrophotometry and its mineralization is valued by measuring the chemical oxygen demand (COD). The influence of several parameters are studied.

References

Valorization of marine biomass for Nickel ion removal from aqueous media

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Activated carbons obtained from two algal species, green algae (GAAC) and brown algae (BAAC) have been examined for nickel ion removal from aqueous solution. Activation was achieved by impregnating both algae separately in phosphoric acid with concentrations ranging from 20 to 85 % and heating the algae-acid mixture starting from 600 to 800 °C which had significant effect on the BET surface area with experimental conditions such as impregnation time, solution pH, adsorbent dose and pyrolysis temperature and attained a value of 1400 and 1144m²/g for the green and brown algae respectively. Developed samples have been characterized by IRFT, BET surface area analysis, pH_zpc, and methylene blue index and iodine number. Batch adsorption tests were performed and the experimental data analyzed using the Langmuir and Freundlich models. The estimated adsorption capacities of Ni²⁺ from the fitting of the Langmuir model to the equilibrium data are 64.51 and 91.70 mg/g brown and green algae respectively in comparison to 6.30 mg/g obtained by the as supplied Merck commercial activated carbon (Merck-AC). Kinetics applied to the experimental data showed that pseudo second order is more representative. The activated carbon prepared showed substantial capability to adsorb nickel ion from aqueous solutions.

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Acknowledgement (optional) - The authors thank the National CNEPRU project (Mostaganem University) E02220070003-01/01/2010 of the Ministry of Higher Education for the financial support.
Ecotoxicological evaluation of technology-critical elements

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During last two decades the use of technology-critical elements (TCEs) such Ga, Ge, In, Nb, Ta, Ti, Pt, Pd, Rh, Os, Ir, Ru, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, have significantly increased and, as a result, the anthropogenic emissions of these elements to the environment also proliferate [1]. Moreover, these trace elements may enter into the ground- and surface water in the more mobile and bioavailable forms than naturally occurring ones. However, our knowledge on biological role, ecotoxicity and bioaccumulation potential of TCEs is very limited since most of these elements have been involved in the technological circulation for relatively short time. In the current study, ecotoxicity of five TCEs was studied: gallium - Ga(NO₃)₃, thallium - TlNO₃, praseodymium - Pr₂(SO₄)₃, neodymium - NdCl₃ and gadolinium - Gd(NO₃)₃ & GdCl₃. The overview of the published information showed that environmental hazard of Tl has been extensively studied, but only sporadic ecotoxicological data are available for Ga, Nd and Pr.

The test suite used by us comprised of tests with aquatic organisms representing different trophic levels (freshwater crustaceans Daphnia magna and Thamnocephalus platyurus, marine bacterium Vibrio fischeri, and freshwater duckweed Lemna minor). The highest tested concentration was 100 mg/L (on metal basis).

The bacterium V. fischeri was the most sensitive to investigated TCEs. 30-min EC₅₀ values for Gd, Nd and Pr were very similar (4.5-6.1 mg/L). The average 24/48 h L(E)C₅₀ values for crustaceans varied: Tl (0.1-0.4) >> Gd (11.7–30.1) ≥ Nd (12.5-19.6) ≥ Pr (19.2 – 24.5) > Ga (>100 mg/L), i.e. Tl was the most toxic element. Acute toxicity values for Tl obtained in the current study are in agreement with earlier published results showing reliability of our experimental toxicity data.

The lanthanides (Gd, Nd, Pr) demonstrated very similar toxicity to all aquatic crustaceans. Interestingly, the toxicity of Tl, Gd, Nd and Pr to duckweeds was comparable to the toxicity of these TCE to crustaceans, but Ga was significantly more toxic to duckweed Lemna minor (7 d LC₅₀ ~ 1 mg/L).

It is generally acknowledged that aquatic plants remarkably bioaccumulate trace metals even if exposed to low concentrations. According to REACH Directive [2], a substance fulfils the bioaccumulation criterion when bioconcentration factor, BCF, exceeds 2000). However, bioconcentration factors (BCFs) for Ga, Gd, Nd and Pr obtained in the current study for duckweeds exposed to different metal concentrations (0.01, 0.1, 1 and 10 mg/L) did not exceed 1000.

References


Acknowledgement - This research is supported by Estonian Ministry of Education and Research (target-financed theme IUT23-5 and PUT748)
A “counter-intuitive” approach to examining free energies of sorption of ionizable organic compounds: removing the impact of solute–bulk solvent interactions

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Sorption of ionizable organic compounds (IOCs) from solutions is of great significance in multiple industrial and environmental processes, e.g., such as extraction and separation of chemical mixtures, water purification, ion exchange, accumulation of IOCs in soils and sediments, transport of organic compounds in porous media and spreading of organic contaminants in various environmental compartments. Understanding of IOC sorption mechanisms is complicated by solute speciation in solutions such that different sorption mechanisms of solute molecules and ions have to be considered. One common approach for elucidating contributions of different species to the overall measured IOC sorption involves determining sorption isotherms at varied pHs. However, there are multiple cases when understanding the pH effect on sorption of IOCs is not straightforward (e.g., due to pH-dependent ionization of surface functional groups) or the pH-dependent measurements are even hardly possible (due to the presence of buffering components, such as calcium carbonate in soils, which cannot be removed without damage of a sorbent matrix). Importantly, even when contributions of non-ionized and ionized species to the thermodynamics of the overall IOC sorption from solution are determined, they are all affected by interactions of species with bulk solvent which “mask” actual interactions occurring in a sorbed state. In the case of sorption thermodynamics of non-ionic solutes (and similarly to that in solvation/dissolution thermodynamics), this problem is resolved simply by changing the initial state in the compound transfer. For this, the transfer of a compound from (aqueous) solution to (hydrated/solvated) sorbent is converted to the transfer from the gas phase [or “inert solvent”] to the same solvated sorbed state [1,2]. The conversion is carried out by using the data on equilibrium distribution of a sorbing non-ionic compound between the gas phase (inert solvent) and water. This conversion of sorption isotherms means re-defining the initial state when the final (hydrated/solvated, sorbed) state is not changed. However, such a conversion of the sorption data/isotherm is not obvious in liquid-phase IOC sorption.

This presentation describes a novel and “counter-intuitive” approach [3] formulating the differential Gibbs free energy of IOC sorption in such a way that the initial thermodynamic state of the sorption process is the solution reference state associated with a non-ionized form of IOC. The final state is an actual sorbed state of IOC which is equilibrated with the real solution and allows any types of IOC-sorbent interactions including IOC ionization in a sorbed state and/or ion exchange. Hence, IOC ion-bulk solvent interactions are excluded from consideration. These differential Gibbs free energies of sorption may be determined without separating the whole IOC sorption into the contributions of different species. However, if such a separation is possible, then, the differential Gibbs free energy of the whole sorption may be divided into the two quantifiable steps: (1) a transfer of neutral IOC molecules from the infinitely diluted solution reference state to a sorbed state, and (2) if applicable, turning on the sorbed IOC ion-sorbent interactions of any type. Further, the suggested definition of the sorption process makes possible the elimination (or minimizing) of IOC-bulk solvent interactions, by converting the molecular IOC solution reference state to another molecular reference state in an inert medium that is in the gas phase or, in some cases, in relatively inert solvents, e.g., saturated hydrocarbons. Thus, the differential Gibbs free energies of sorption may be “cleaned” of IOC-bulk solvent interactions and, therefore, can be examined in terms of organic sorbate structure effects, with the focus on interactions in a sorbed state. This concept is illustrated by examining the data on sorption of trifluoroacetic vs. acetic acids, and of the representatives of pharmaceuticals and personal care products (triclosan, gemfibrozil, galaxolide) on some natural sorbents.

References

The electrochemical deposition of nickel from Watt’s bath

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In this work, nickel deposits were produced by direct current electrodeposition on nickel substrates. Electrodeposition used a free-additive Watt’s bath. No additives were used in order to limit the incorporation of pollutants resulting from surface adsorption or electro-activity of these compounds.

The optimum conditions of deposition were established and the influence current density on the grain size, surface morphology and crystal orientation was determined.

The study showed that the current density has a remarkable influence on the surface morphology of electrodeposited Ni.

Nickel coating has been investigated by Scanning electron microscopy and X-ray diffraction. Cyclic voltammetry was also used to gain information on the general behaviour of the deposition process.

References
Free Zn concentration in various media with dispersions of ZnO nanoparticles.

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The large number of commercial products that use nanoparticles (NPs) has led to intense research investigating their potential effects on human health and environmental impact. The toxicological and environmental impact of engineered nanoparticles (NPs) in various media depends on a number of physicochemical phenomena including those taking place at the particle-media interface, which are particularly relevant due to the high specific surface area of these materials. These phenomena determine the behaviour of the NPs (solubility, aggregation, precipitation etc.) at the pH, salinity, and composition of the medium.

In the particular case of ZnO NPs, parameters such as particle size, temperature and solute adsorption may influence the release of free Zn$^{2+}$ ions, which, in turn, play an important role in the toxic effects of these NPs. The new technique AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has been used to obtain in situ information on the equilibrium and dynamic release of Zn$^{2+}$ ions in dispersions of ZnO NPs in various media [1-4] without the requirement of solid-liquid separation (as in conventional solubility techniques [5]).

In this work, various media have been considered: a) 0.1 M KNO$_3$ or KCl aqueous solutions; b) growth media (DMEM) held under identical conditions to those employed for cell culture (37 °C, 5% CO$_2$ and pH 7.68); and c) artificial saliva (37 °C and pH 6.84). The stability, agglomeration state and particle size distributions of the samples was monitored by UV-vis spectroscopy and Dynamic Light Scattering.

References

Acknowledgements - The authors thank support from European Union Seventh Framework Programme (FP7-NMP.2012.1.3-3) under grant agreement no. 310584 (NANoREG), and from the Spanish Ministry of Education and Science (Projects CTM2012-39183 and CTM2013-48967).
Removal of chlorpyrifos from waters using endocarp of *Euterpe oleracea* Mart. chemically modified

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In rich Amazon rainforest, the acai (*Euterpe oleracea* Mart.) appears as a native palm tree, which occurs in large fields in the Amazon estuary. The state of Pará is the main natural center of dispersion of that palm, being the most productive, both in fruits and as derivatives. One of the organophosphate class of pesticides is chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridylphosphorothioate) classified by the Brazilian National Health Surveillance Agency (ANVISA) as organophosphate-chlorinated insecticide, acaricide and formicide authorized only for agricultural use and being applied in crops such as cotton, bananas, potatoes, coffee, citrus, beans, apples, corn, soybean, tomato, sorghum and wheat. The aim of this work was to obtain natural and chemically modified adsorbents with high adsorptive capacity for removal of chlorpyrifos on water resources.

Figure 1. Molecule structure of chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridylphosphorothioate)

The pesticide solutions were prepared from certified standards of 0,0-diethyl O-3,5,6-trichloropyridine-2-ill phosphorothioate (Chlorpyrifos®). The response surface methodology was used to obtain an empirical mathematical model to represent the influence of factors mass of adsorbents (endocarp acai *in natura* and chemically modified with NaOH, H₂O₂, H₂SO₄) and pH of the solution in the adsorption process of chlorpyrifos. To verify the optimal conditions for adsorption, mass tests were performed, using for this, increasing amounts of adsorbent material (250; 396.4; 750; 1103.6; 1250 mg) at five pH conditions (3.0, 3.6, 5.0, 6.4 and 7.0). Thus, in Erlenmeyer flasks of 125 ml, the masses of adsorbent were added and coupled with fixed volumes of 50 ml of each aqueous solutions fortified with pesticide. At the end of each adsorption test, all Clorpirifós® concentrations were determined by Gas Chromatography with an Electron Capture Detector (GC-ECD).

Table 1. Planning matrix CCRD with quadruplicate at the midpoint in their coded and real values.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Variables</th>
<th>Q_{ads} (ug g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X₁ mass (mg)</td>
<td>X₂ pH</td>
</tr>
<tr>
<td>1</td>
<td>-1 396.39  -1</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>1 1103.6   -1</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>-1 396.39  1</td>
<td>6.4</td>
</tr>
<tr>
<td>4</td>
<td>1 1103.6   1</td>
<td>6.4</td>
</tr>
<tr>
<td>5</td>
<td>0 750      0</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>-1.41 250  -1</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>0 750      1.41</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>1.41 1250  0</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>0 750      -1.41</td>
<td>3</td>
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<tr>
<td>10</td>
<td>0 750      0</td>
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<tr>
<td>11</td>
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<td>5</td>
</tr>
<tr>
<td>12</td>
<td>0 750      0</td>
<td>5</td>
</tr>
</tbody>
</table>

The best adsorption conditions were observed when used 396.39 mg at pH 3.6 for CA *in natura* (Q_{ads} = 124.14). For the materials modified with H₂O₂, H₂SO₄ and NaOH, the best results were obtained with 250 mg at pH 5.0 in which Q_{ads} is respectively 94.28, 90.30, 52.62 ug g⁻¹. The lowest values of Q_{ads} were found when using 1250 mg at pH 5.0 for the modified adsorbent with NaOH, which was 7.72 ug g⁻¹. For adsorbents CA *in natura*, modified with H₂O₂ and H₂SO₄, the lowest results were found when used mass of 750 mg and pH 5.0.

Acknowledgement - The authors would like to thank the CNPq for its funding and research productivity and the CAPES for the postgraduate scholarship.
Zinc complexing ligands in seawater, river water and peat land water from natural, agricultural and industrial sources in South East Asia: Elucidating humics, ligands and bioavailable metals in complex systems

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Organic complexing ligands dominate the chemical speciation of Zn in seawater globally, affecting its bioavailability and regulating its micronutrient role. We have shown that intermediate water masses in the West Pacific indicate a connection between point sources related to marginal seas, riverine matter, benthic fluxes, and continental shelves, with ligand concentrations and binding strengths evolving along water mass trajectories.

Here we will present results from recent studies in tropical South East Asia that explore rivers in pristine peatland areas in Borneo, and rivers near and around agricultural and industrial anthropogenic influence in Borneo, Singapore and Malaysia, with the aim of elucidating the importance of relatively fresh natural and agricultural land-based plant material and industrial anthropogenic material in the organic matter mix that the ligands are a part of. These results track the ligand concentration and binding strength of different sources of Zn complexing ligands obtained using ASV and modern comprehensive mathematical methods. We will compare records of humic substances from coral cores near the mouth of these rivers, with the goal of ascertaining a possible link of humic substance concentrations and metal complexing ligands in the region. We will compare the results from these large sources of organic matter with samples from a transect across the Malacca Straits that reflects what could be transported further out, with the ligands observed in continental shelves, where the organic matter has suffered biochemical processes, with previous analysis of ligands observed in the West Pacific, after decades of bacterial respiration while travelling along water masses. We aim to compare these ligands in order to assess the relevance of these sources of complexing ligands to regulate regional and global distribution of Zn ligands and its bioavailable concentrations.
Effect of high carbon loading by surface-modified AC on flow-electrode capacitive deionization

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Flow-electrode capacitive deionization (FCDI) is a novel CDI system based on membrane CDI (MCDI).¹ Flow electrode means carbon slurries consisted of porous carbon (activated carbon, AC) and NaCl electrolyte. As the salt adsorption efficiency depends on porous carbon-loading amount,² it is nessesary to modify hydrophobic surface to hydrophilic one in order to improve the wettability for high carbon loading because hydrophobic AC is easy to aggregate in aqueous environment. In this study, we fabricated the surface-modified AC suspensions with ionic head-groups and confirmed the desalting effect according to the carbon concentrations. In particular, for anode (AC-N) and cathode (AC-S), we chose the trimethyl ammonium and sulfonate, respectively, and synthesized AC particles covered with the ionic-head groups through radical polymerization. The coating layer was about 5 nm, irrespective of anion and cation. Compared to bare AC, the surface-modified AC became hydrophilic. Moreover, it was possible to increase the carbon concentration up to 35% due to electrostatic repulsion and as a result, the current as well as the desalting efficiency increased up to 900 mA as well as 27% (Figure 1). Therefore, we expect that the surface-modified AC electrode can be used as a dispersant and flow electrodes.

Figure 1: The results of deionization performance: profiles of (a) NaCl conductivity changes and (b) current

References


Mn-substituted magnetic iron (III) oxyhydroxides for oxidative adsorption of arsenic in aqueous solution

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Iron oxyhydroxide substituted with Mn (MSF) was prepared and characterized, and its adsorption properties for As(III) and As(V) were evaluated in a series of experiments. Four synthetic MSF samples with different molar ratios of Mn:Fe (0, 10, 30, and 50% Mn) were prepared by hydrolysis of Fe(II) ions and Mn(II) ions under alkaline conditions followed by rapid oxidation with H₂O₂. Synchrotron based powder X-ray diffraction patterns were collected on the beamline 9B (HRPD) at Pohang Accelerator Laboratory (PLS-II) in Korea. Crystal structure analysis using Rietveld method revealed that the crystal structures of MSF materials resemble those of feroxyhyte (δ’-FeOOH), with the unit cell volume and a-axis lattice parameter proportionally decreasing with increasing Mn-substitution, resulting in the formation of a δ-(Feₓ₋ₓ, Mnₓ)OOH-like structures. Zeta potential analysis of MSF showed that the particles became negatively charged with an increasing Mn ratio. MSF with a high molar ratio of Mn showed high oxidative capacity that enables oxidation of Cr(III) to Cr(VI) or As(III) to As(V), while the composite had relatively low adsorption capacities for As(III) and As(V). MSF containing 10% Mn removed 72.5-89.2% of total adsorbed arsenic species within the first 70 min in the range of initial concentrations of 19.5-96.7 As(III) mg L⁻¹ and 19.4-98.0 As(V) mg L⁻¹. The oxidative capacity of MSF measured using the Standard Chromium Net Oxidation Test increased proportionally from 0.02 to 18.44 mmol/kg with increasing Mn-substitution, but magnetic susceptibility decreased significantly from 157.5 to 0.8 mSI. These results showed that magnetic Mn-substituted iron oxyhydroxide, developed at the optimal molar ratio of Fe and Mn, could oxidize contaminants and adsorb arsenic species in aqueous solution, and could easily be recovered by magnetic separation after use.
Determination of free Indium concentrations and lability degrees in aquatic solutions by electroanalytical techniques

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AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) is an electroanalytical technique designed for the determination of free metal ions in sample solutions such as seawater, river water, dispersion of nanoparticles and soil extracts [1]. Indium is one of the critical elements, widely used in electronic devices, which can eventually leak towards the environment causing several problems. Despite its increasing use, there are many unresolved aspects of the behaviour of free Indium in various systems which require an accurate study of its speciation and availability [2].

The implementation of AGNES with mercury electrodes requires amalgamating elements such as Zn, Cd, Pb, Sn or In. Nevertheless, due to some irreversibility of Indium on the Hg electrode, it is not possible to compute directly the potential associated to a given gain, leading us to perform a new calibration method for the determination of [In3+] taking into account the charge and the volume of the Hg drop.

In general, the deposition times required to reach AGNES equilibrium are slightly increased due to In irreversibility. The collapse of normalized trajectories (i.e. time profiles) indicates the validity of AGNES key equation and the proportionality between gain and deposition time.

Speciation results in the system Indium+Nitrilotriacetic acid with AGNES agree with computations using database NIST 46.6. However, the evolution of free Indium when increasing amounts of the ligand oxalate are added indicates that the values of the stability constant in NIST 46.6 [3] are not as accurate as those of Vasca et al. [4].

A new strategy, called Accumulation under Diffusion Limited Conditions (ADLC), can be applied to compute the lability degree of complexes. The lability degree is strongly linked to the availability of this element as it describes the contribution of the complexes to the overall uptake flux. The use of highly labile complexes (such as those of oxalate) allows for a dramatic reduction of the deposition times at huge gains. For instance, in the system oxalate+In at pH 3, equilibrium for a gain larger than 300000 was attained in just 25 seconds retrieving [In3+] = 3.71×10^{-10} mol L^{-1}. In precipitated solutions at pH 5.6 (where the free Indium concentration is fixed despite the addition of the helping oxalate), [In3+] = 1.87×10^{-11} mol L^{-1} was determined.

References
Understanding membrane fouling in produced water treatment

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Produced water is the largest waste stream generated by oil and gas production. It is a complex oil-in-water emulsion of organic and inorganic compounds, which are present in both a dispersed and a dissolved state. Before this produced water can be re-injected, discharged or re-used as irrigation water or industrial water, the water has to be treated\cite{1}. A large challenge is posed by the smallest (<10 µm) and most stable oil droplets. Membrane technology is able to remove those oil droplets, but membranes suffer from fouling, leading to a flux decline. Current research on produced water treatment by membranes is mainly focused on improving existing processes and developing fouling-resistant membranes. Multiple investigations have determined the importance of different factors (such as emulsion properties and operating conditions) on the fouling process, but understanding the background of fouling is largely absent\cite{2}. Studying the interactions of oil droplets in an emulsion with the membrane surface is essential for understanding the fouling process and thus come to new solutions for produced water treatment with membranes.

To understand the interaction of the oil droplets in produced water with membrane surfaces, we use a model system of a modified glass slide that mimics the membrane surface in a flow cell under a microscope (See Figure 1). By filling the cell with an oil-in-water model emulsion we can study the adhesion and spreading of the droplets to the surface, as well as the removal of the droplets from the surface under increasing shear forces.

![Figure 1: Schematic representation of the flow cell set up with laminar flow at variable flow rates with A) replaceable glass plate, B) silica plate, C) Microscope objective (Reproduced from [3])](image)

The behavior of the oil droplets at model interfaces is the directly compared to filtration experiments on polymeric membranes with similar surface chemistry using the same model emulsion. We demonstrate that these complimentary techniques allow clear insight into the influence of different factors on membrane fouling in produced water treatment.

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Bio-elements bioavailability from the blanched and pickled chanterelle

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We studied bioavailability of cobalt, copper, iron, magnesium, manganese, nickel and zinc from the blanched and pickled chanterelle Cantharellus cibarius using an in vitro model. Mushrooms were collected in Poland, blanched for 5 and 15 min in boiling water and a part of them were pickled using a diluted vinegar. The method of metallic elements bioavailability analysis from culinary processed samples of mushrooms included two successive processes of stomach and intestinal digestion tract. The in vitro bioavailability model based on the unified bioaccessibility method (UBM) proposed by the Bioaccessibility Research Group of Europe (BARGE) was used. Final determination of elements was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES). The higher percentage bioavailability was usually obtained for samples subjected to gastric digestion (Fraction 1) than the gastrointestinal digestion (Fraction 2) both for the blanched and pickled C. cibarius.

Acknowledgement - This study was financially supported by the Polish National Science Centre (NCN) grant DEC-2012/05/N/NZ9/01561.
Investigations on leaching of mercury from the blanched and pickled mushrooms

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We studied leaching of mercury from the chanterelle *Cantharellus cibarius* Fr. and *Amanita rubescens* Pers., mushrooms after blanching (short time boiling) and pickling. Mercury was determined using the validated method by cold vapour - atomic absorption spectroscopy (CV-AAS). Fresh chanterelle blanched for 5 min in boiling water lost 13% of accumulated mercury ($p < 0.05$), while blanched for 5 min and further pickled with solution of a vinegar lost 21% of mercury. Fresh chanterelle blanched for 15 min in boiled distilled or mineral water lost 12-13% of mercury, while blanched for 15 min and pickled with a solution of a vinegar lost 15-19% of mercury. Chanterelle deep frozen (-25°C) when blanched for 15 min in boiled distilled or mineral water lost 33-36% of mercury ($p < 0.05$), while blanched for 15 min in boiled distilled or mineral water and further pickled lost 37-39% of mercury ($p < 0.05$). Fresh fruiting bodies of edible *A. rubescens* blanched for 15 min in boiling distilled water or blanched and further pickled lost around 50% of accumulated mercury ($p < 0.05$).

Funding: This study was financially supported by the Polish National Science Centre (NCN) grant DEC-2012/05/N/NZ9/01561.
Elaboration of chitosan micro-beads by prilling method for water treatment

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Chitosan micro-beads were elaborated by a granulation jet vibrating method called “prilling”. The designed pilot (Figure 1) allows to form porous hydrogel beads with a given size, by formation of droplets of a polysaccharide solution by using vibration and passing through a calibrated nozzle, and then the drop in a gelling bath. The device allows to quickly produce sufficient quantities of adsorbent material for a subsequent transposition to the industrial scale. To optimize the process, different parameters were varied in order to obtain chitosan micro-beads with different structural properties and porosities.

![Figure 1: Schematic representation of the “prilling” device:](image)

The nature and concentration of the acids used to solubilize chitosan were studied and have shown an importance regarding chitosan hydrogels’ mechanical strength. Best results were obtained with acetic acid, formic acid and citric acid. Concentration of chitosan has shown a great importance during the “prilling” process because of the change in the gel viscosity, which influenced on the mechanical strength of the formed beads. The minimum mass concentration to form beads with satisfying properties was determined. Gelling bath composition was varied to ensure a fast gelling before the deformation of the beads and to obtain high porosities. Our study has demonstrated that a too low concentration in sodium hydroxide leads to weak mechanical strength and the addition of ethanol in the gelling bath enhances the specific surface area of the lyophilized beads.

**Acknowledgement** - The authors would like to thank the “Rhône-Alpes region” -France-, for the financial support.
Iron based catalysts supported on activated carbon from banana spike for the treatment of waste water from textile industry by a Fenton process

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The catalytic effect of iron based nanoparticles supported on a mesoporous activated carbon (referred to AC) prepared from banana spike was tested on a solution of rhodamine B (RhdB) used as a model pollutant of textile industry waste water [1]. These AC-Fex (x= 3, 7 or 11) heterogeneous catalysts [2] were prepared by impregnation of the activated carbon (SBET = 896 m2/g) by x weight % of iron sulfate (FeSO4·7H2O) in water solution, followed by drying at the rotary evaporator and by calcination at 350°C. The presence of iron based nanoparticles was confirmed by TEM (Transmission Electron Microscopy) and SEM (Scanning Electron Microscopy). Characterizations by X-ray Photoelectron Spectroscopy and X-ray microanalysis analyses have confirmed the presence of iron linked with oxygen, phosphorus and sulfur elements, and oxygenated surface groups, phosphorus and sulfur on the AC. The pore size distribution obtained by nitrogen adsorption at 77 K has shown that the pores of the activated carbon are occupied by the iron based nanoparticles reducing the adsorption phenomena of the dye. The catalysts were tested in batch reactors for the removal of the RhdB (C0 =50 mg/L), in the presence of 8 mmol/L of H2O2. The residual RhdB was analyzed by UV-visible spectrophotometry. 96 % of RhdB are removed for 3 hours at pH 4.3 using 0.26 g/L of AC-Fe11 catalyst yielding to the mineralization of RhdB corresponding to a decrease of 60% of the total organic carbon (Figure 1). The solubilized iron concentration value is less than 0.5 mg/L.

Figure 1: Removal of the rhodamine B versus time by the heterogeneous Fenton process

References
How dissolved organic matter affects interactions of atrazine and lamotrigine with carbon nanotubes

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The presence of organic pollutants in the environment is worrisome. In recent years, pesticides, pharmaceuticals and personal care products have been frequently detected in aquatic environmental systems. Among these pollutants, the herbicide atrazine and the anticonvulsant drug lamotrigine have both been detected at high concentrations in the environment. For the future safety of our water systems, efforts must be invested in expanding our knowledge on the behavior of such pollutants in the aquatic environment and in examining prospective applications for their removal from water.

Carbon nanotubes (CNTs) are known as efficient adsorbents and are being widely investigated for their potential use in water treatment technologies. Furthermore, in light of their increasing use they will inevitably be released into environmental systems where they may interact with additional substances such as organic pollutants and dissolved organic matter (DOM). DOM is an integral part of environmental systems and plays a key role in adsorption of organic pollutants. Even though adsorption of organic compounds by CNTs has been widely researched, the effects of DOM on adsorption under different solution chemistries have been rarely addressed. Therefore our main objective was to systematically research the influence of DOM on atrazine and lamotrigine adsorption by CNTs in varying solution conditions and introduction stages of DOM.

This study shows that atrazine and lamotrigine compete over the same adsorption sites. However atrazine was a far more effective competitor than lamotrigine, suggesting there are adsorption sites preferentially occupied by atrazine. The presence of DOM greatly suppressed adsorption of both pollutants. For example, in the midst of their adsorption isotherms, adsorption of atrazine decreased by 94%, and that of lamotrigine by 69%, at high concentration of DOM, respectively. This may be attributed to competition or blockage of adsorption sites by DOM. However, decrease in adsorption of lamotrigine may also be allocated to the formation of a stable DOM-lamotrigine complex with lower affinity to the CNTs. Increased stability of lamotrigine (and not atrazine) was demonstrated by its enhanced solubility in the presence of DOM (the solubility of lamotrigine was increased by up to 70% in DOM solution).

This study will enhance our understanding of interactions between organic compounds and CNTs in environmental systems containing DOM. Furthermore, our findings will ameliorate the potential application of CNTs in organic pollutant removal technologies.
Heavy metal pollution characteristics and its effects on soil enzyme activities in lead-zinc mining area

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Soil microbes play an important role in soils and serve a sensitive indicator to response environmental stressors, such as heavy metals. Therefore, enzyme activities, substrate induced respiration (SIR), mineralizable N, and community level physiological profiles are used for biosafety assessment in the metal-contaminated soils. The heavy metal pollution characteristics and soil enzyme activity of YinDongLiang lead-zinc mining area in Shanxi Province Baoji city were studied based on the outdoor sampling and laboratory analysis. The correlation analysis of soil physiochemical properties and soil enzyme activity showed that the basic physical and chemical properties and soil enzyme activity are significantly correlated; Heavy metals and soil enzyme activity is analysed by the method of multivariate regression, which showed that there is a significant correlation between compound pollution of heavy metals and soil enzyme activities. Furthermore, the effect of compound pollution on soil enzyme activity is depend on the type of the heavy metal pollution degree; At the same time, the compound pollution levels of soil enzyme and heavy metal were carried on by the principal component analysis to establish the ration quota system of soil enzyme activities.

Acknowledgement - The authors thank the Natural Science Foundation of China (Grant Nos. 41201226) for the financially support.
Electrochemical degradation of 4-hydroxyphenylacetic acid in sulfate solutions using a BDD/air-diffusion cell

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The decontamination of olive oil mill wastewater (OMWW) is a matter of great concern in Spain as the country with largest world production of olive oil. The large variety of recalcitrant substances contained in OMWW is a drawback, since it is difficult to remove them for recycling the large volumes of water typically generated. 4-Hydroxyphenylacetic acid (4-HPA) is a main component of OMWW [1]. This communication presents the effective remediation of acidic sulfate solutions of 4-HPA by electrochemical advanced oxidation processes (EAOPs) including anodic oxidation with electrogenerated H₂O₂ (AO-H₂O₂), electro-Fenton (EF) and UVA photoelectro-Fenton (PEF). In these EAOPs, the main oxidants are the hydroxyl radicals (·OH) generated in situ at the BDD anode in all cases and, additionally, from Fenton’s reaction in EF and PEF [2,3]. In PEF, the degradation is expected to be accelerated by the photolysis of several intermediates under UVA irradiation.

Experiments were carried out in a stirred tank reactor with a 3 cm² boron-doped diamond (BDD) anode and a 3 cm² air-diffusion cathode for continuous production of H₂O₂ from the two-electron reduction of O₂ from injected air. 4-HPA (98% purity) was supplied by Sigma-Aldrich. Solutions of 100 mL with 0.21-2.1 mM of this compound in 0.050 M Na₂SO₄ as background electrolyte at pH 3.0 and 35 ºC were comparatively treated by AO-H₂O₂, EF and PEF at constant current density (j) between 16.7 and 100 mA cm⁻². A concentration of 0.50 mM of Fe²⁺ was added as catalyst of Fenton’s reaction to the solutions for the EF and PEF processes. The latter EAOP was performed under UVA irradiation with a 6 W lamp.

The concentration decay for the acidic 4-HPA solutions was followed by reversed-phase HPLC. While the substrate was completely removed in 300-360 min by AO-H₂O₂, less than 60 min were needed in EF and PEF, both showing similar removal rates. This demonstrates the higher oxidation ability of OH originated from Fenton’s reaction compared to that formed at the BDD surface. The TOC abatement of the treated solutions increased in the sequence AO-H₂O₂ < EF < PEF under comparable conditions. For example, for 0.21 mM 4-HPA at 16.7 mA cm⁻², TOC was reduced by 69%, 85% and 97% for the above processes in 360 min. The decrease in substrate concentration and the increase in j yielded a higher removal of 4-HPA and its oxidation products, as a result of the smaller organic load and the generation of larger amounts of oxidizing OH radicals, respectively. Mineralization current efficiencies were determined for all the assays, attaining maximum values near 90% for the most powerful PEF treatment (i.e., 2.1 mM 4-HPA solution treated at 33.3 mA cm⁻²). Aromatic intermediates were identified by GC-MS and final short-linear carboxylic acids were quantified by ion-exclusion HPLC. The quicker removal of oxalic acid from photodecarboxylation of their Fe(III) complexes by UVA light explained the superior oxidation ability of PEF. Based on the detected products, a plausible reaction sequence for 4-HPA mineralization is proposed.

References

Acknowledgement: The authors thank the financial support from MINECO (Spain), under the project CTQ2013-48897-C2-1-R co-financed with FEDER funds, and the scholarship awarded by Senescyt (Ecuador) to N. Flores.
Interactions between Residual Ionizable Pharmaceutical Micropollutants in Treated Wastewater and Metal Oxides in Soil

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In the United States and many other countries around the world, contamination of the environment by pharmaceuticals is becoming an issue of growing concern. Pharmaceuticals and other ionizable micropollutants can enter the environment through the discharge of effluent from wastewater treatment plants (WWTPs) as most secondary treatment WWTPs are not designed to remove them. Moreover, levels of pharmaceuticals in wastewater are highly variable because people with varying ailments of different severities consume medicine either routinely or episodically. Furthermore, new classes of pharmaceuticals are introduced in the market every day, making the composition of ionizable organic compounds in wastewater even more complex. Other pathways for the introduction of human-derived micropollutants into the environment is through the discharge of septic system effluent and through the reuse of biosolids derived from sewage sludge. These contaminate surface water, groundwater and soil. Apart from these pathways, micropollutants can also enter the environment through the runoff from animal rearing operations, which commonly use pharmaceuticals to control disease and/or promote growth.

The main objective of this research is to study the fate and transport of ionizable organic micropollutants, including pharmaceuticals, in treated municipal wastewater and to, specifically, understand the interactions between metal oxides commonly found in soil (e.g. titanium (IV) oxide, magnesium oxide, iron (III) oxide, aluminum oxide and silicon oxide) with the residual micropollutants. The adsorbents were characterized by SEM (for morphology), EDX (elemental analysis), XRD (crystallinity), Zeta potential (surface charge), dynamic light scattering (aggregation in water) and nitrogen adsorption/desorption (surface area and porosity). The batch adsorption experiments were performed to understand the adsorption of 22 selected ionizable micropollutants listed in Table 1 on metal oxides. The overall adsorption behaviour of ionizable compounds was examined with emphasis on the effects of ionization on adsorption. The pH of background aqueous system was varied to completely and/or partially ionize the sorbent pharmaceuticals. The micropollutants in the aqueous phase were quantified by liquid chromatography.

Table 1: List of ionizable micropollutants studied for the adsorption on metal oxides

<table>
<thead>
<tr>
<th>No.</th>
<th>Micropollutant</th>
<th>pKa</th>
<th>log Kow</th>
<th>No.</th>
<th>Micropollutant</th>
<th>pKa</th>
<th>log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17-alpha-Ethynylestradiol</td>
<td>10.33 (strongest acidic) and -1.7 (strongest basic)</td>
<td>3.67</td>
<td>12</td>
<td>Erythromycin USP</td>
<td>8.88 at 25°C</td>
<td>3.06</td>
</tr>
<tr>
<td>2</td>
<td>17-beta-Estradiol</td>
<td>10.33 (strongest acidic) and -0.88 (strongest basic)</td>
<td>4.01</td>
<td>13</td>
<td>Estrone</td>
<td>10.33 (strongest acidic) and -5.4 (strongest basic)</td>
<td>3.13</td>
</tr>
<tr>
<td>3</td>
<td>4-para-Nonylphenol</td>
<td>10.31 ; -5.44</td>
<td>5.76</td>
<td>14</td>
<td>Fluoxetine HCL</td>
<td>9.8 (strongest basic)</td>
<td>3.32</td>
</tr>
<tr>
<td>4</td>
<td>4-tert-Octylphenol</td>
<td>10.33 at 25°C</td>
<td>4.12</td>
<td>15</td>
<td>Gemfibrozil</td>
<td>4.5 (carboxylic acid)</td>
<td>4.77</td>
</tr>
<tr>
<td>5</td>
<td>Acetaminophen</td>
<td>9.38</td>
<td>0.46</td>
<td>16</td>
<td>Ibuprofen</td>
<td>4.91</td>
<td>3.97</td>
</tr>
<tr>
<td>6</td>
<td>Bisphenol A</td>
<td>9.6</td>
<td>3.32</td>
<td>17</td>
<td>Naproxen</td>
<td>4.15</td>
<td>3.18</td>
</tr>
<tr>
<td>7</td>
<td>Caffeine</td>
<td>10.4 (at 40°C)</td>
<td>-0.07</td>
<td>18</td>
<td>Primidone</td>
<td>11.5 (strongest acidic) and -6.2 (strongest basic)</td>
<td>0.91</td>
</tr>
<tr>
<td>8</td>
<td>Carbamazepine</td>
<td>13.9</td>
<td>2.45</td>
<td>19</td>
<td>Progesterone</td>
<td>18.92 (strongest acidic) and -4.8 (strongest basic)</td>
<td>3.87</td>
</tr>
<tr>
<td>9</td>
<td>Ciprofloxacin HCL</td>
<td>pKa = 6.09 (carboxylic acid group); pKa = 8.74 (nitrogen on piperazinyl ring)</td>
<td>0.28</td>
<td>20</td>
<td>Sulfamethoxazole</td>
<td>pKa1 = 1.6; pKa2 = 5.7</td>
<td>0.89</td>
</tr>
<tr>
<td>10</td>
<td>Diclofenac sodium salt</td>
<td>4 (strongest acidic) and -2.1 (strongest basic)</td>
<td>0.7</td>
<td>21</td>
<td>Testosterone</td>
<td>19.09 (strongest acidic) and -0.88 (strongest basic)</td>
<td>3.32</td>
</tr>
<tr>
<td>11</td>
<td>Erythromycin USP</td>
<td>8.88 at 25°C</td>
<td>3.06</td>
<td>22</td>
<td>Triclosan</td>
<td>7.9</td>
<td>4.76</td>
</tr>
</tbody>
</table>
Degradation of toxic polycyclic substances by electrochemical oxidation

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Water is a necessary element for life on earth and the quantity and quality of water resources relates directly to the quality of life. Unfortunately, good quality water is very limited. According to UNEP, around two billion people do not have access to good quality water, are forced to use dirty water for every day needs and suffer. Several million people die every year from diseases directly related to the use of dirty water.

In addition to that discharge of contaminated water destroys the quality of water in rivers and lakes. Major polluter industries like pulp and paper production, textile industry etc. produce huge quantities of wastewater containing polycyclic non biodegradable substances. For example, in textiles, around 200 L of wastewater are produced per Kg of fiber processed. Given that the annual World fiber supply is estimated to around 70 million tones more than 10 billion m³ of wastewaters are produced annually just by textile industry. New effective processes are needed to treat such wastewaters.

Electrochemical oxidation is a promising new process. Laboratory experiments with the most used commercial reactive dyes have been very effective. All polycyclic substances present in the dyes were completely broken. Black, red and blue commercial grade reactive dyes were tested successfully with different anodes and cathodes and in presence of various electrolytes. NaCl, which already exists in real wastewaters was the most effective. Complete discoloration was obtained in 10 min. It was shown by TOC measurement that more than 75% of organic carbon was mineralized and LC-MS measurements have proved that polycyclic substances have been broken completely. The treated water was fed to laboratory bio-reactor and was found to be biodegradable. The cost of the process was comparable or even better than current ineffective practices.

Figure 1: a) Effect of the NaCl on the degree of TOC (solid line) and COD (dashed line) removal of dye RB-19. b) Photos of real wastewater degradation (from a textile industry) with BDD anode.

keywords: electrochemical oxidation, polycyclic substances, discoloration

Acknowledgement: The financial support of this research provided by the following projects: 1) People Programme (Marie Curie Actions) of the European Union’s Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n°612250 (project WaSClean FP7-People-2013-IAAP) as well as 2) Slovak R&D Agency project No APVV-10-0252-WATRIP and 3) NATO SPS Multi-Year Project EAP:SFPP 984403
Regenerable Stimuli Responsive PVP-clay Graft Composites for the Removal of Toxic Oxyanions from Water

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In recent years many studies have reported the development of polymer-clay composite sorbents for specific and high pollutant removal. High affinity of the pollutants to these sorbents frequently causes regeneration and reuse extremely challenging, either due to irreversible binding or due to polymer loss during regeneration. In the current study we aimed to develop a new series of regenerable polymer-clay sorbents based on covalently grafted poly vinylpyridine (PVP) to montmorillonite. Poly vinylpyridine (PVP) is a pH depended polycation and grafting it to a surface yields a reversible coating which extends or collapses upon gaining or losing monomer charge.

Figure 1: schematic oxyanaion removal cycle by regenerable pH responsive grafted PVP brushes

The sorbents were prepared in four stages: 1. Acid activating the clay 2. Covalently grafting 3-aminopropyltriethoxysilane (APS) to the clay (determines grafting density) 3. Surface initiation with 2-bromoisoobutyryl bromide and 4. ATRP of PVP (determines chain length). Brushes density and chain length affect sorbent capacity and “on que” release. The sorbents were characterized by Zeta potential, XRD, FTIR, TGA and XPS measurements. The new grafted clays colloidal size can reversibly change. Composites with relatively dense and long polymer chains can shrink to nearly four times the original size, when solution pH changes from 3 to 8. The collapse of the grafted chains and the loss of surface charge trigger rapid precipitation as the composite suspension is no longer stable. Finally, the removal of oxyanions selenate, arsenic and sulfurous by the sorbents and their regeneration was explored. For a composite with relatively sparse long chains a high selenium capacity of 22.4 mg/ g was reached at a low pH. Selenate release was triggered by increasing pH reaching 90% desorption. Re-activation of the regenerated sorbent was performed by washing it with HCl 2 mM. Re-adsorption of selenate was as high as the first cycle. No polymer desorption was observed.
Formation and properties of inorganic Si-contaminant compounds

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Several studies demonstrate the positive effect of Si fertilizer on the resistance of some plants upon soil contamination. The use of Si fertilizer led to a significant reduction of Pb, Cd and Cu toxicity in crops. One of the possible reasons is the immobilization of contaminants by the formation of contaminant-containing Si phases. The contaminants are bound in these phases in an immobile form and are thus not available for plant uptake. However, this process has not previously been systematically investigated and clarified.

The objective of this work was to characterize the interactions between dissolved silica and metal cations (Pb, Cd and Cu) under natural conditions (ambient temperature and pH 4-6.5) and the precipitated Si-contaminant compounds.

The interactions between dissolved silica (as tetraethylorthosilicate, TEOS) and metal cations (as CdCl₂, CuSO₄ and PbCl₂) were investigated at different initial concentrations (2-50 mM) and metal:Si molar ratios (0.15-1) at ambient temperature and pH 4-6.5. The plant available (adsorbed) and total content of metal cations and Si in the precipitated compounds were determined by extraction with 0.01 M CaCl₂ solution in several time steps (1-48 hours) and total digestion (according to DIN ISO 14869-2 (2003) and VDLUFA (2011) for the samples with Cd). The morphology of the precipitated particles was examined with scanning and transmission electron microscopy (SEM/TEM), they were further characterized by XRD, FT-IR and ²⁹Si-NMR spectroscopy.

The composition of the compounds differed, with 160-365 g kg⁻¹ Si, 290 g kg⁻¹ Pb, 340 g kg⁻¹ Cu and 23 g kg⁻¹ Cd. Copper was incorporated in the amorphous silica structure by forming Si-O-Cu bonds, as indicated by FT-IR spectroscopy (shift of the Si-O stretching vibration towards a lower wave number (1022 cm⁻¹), relative to that in amorphous silica (1100 cm⁻¹)) and ²⁹Si-NMR spectroscopy, where a new signal at -334 ppm was detected after the reaction. This points to immobilization of Cu.

The amounts of Si and metals extracted with 0.01 M CaCl₂ from the newly formed compounds were constant after 24 hours, with 3-4% Si and 0.1-0.8% metal of the total Si and metal content of the respective compound released (except for Cd with a release of 45%). Therefore, Cu and Pb in aqueous solution were predominantly transferred to form, in which they are not available for plants. These preliminary results indicate that the effect of Si fertilization on plant availability of toxic metals might be the consequence of a precipitation reaction, including partial incorporation of the metals in the amorphous silica structure.

References
Use of modified cassava barks as adsorbents of chlorpyrifos from waters

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The rapid urbanization and industrialization of the 20th century resulted in a fast increase in production and use of pesticides, both in agriculture and urban areas, causing big concern on issues related to the various ways that these toxic molecules can cause contamination to the environment. Within a wide range of pesticides used in agriculture, chlorpyrifos is an organophosphate insecticide of broad spectrum, which has been used extensively in the past also in residential environments. Despite its proven effectiveness in pest control, chlorpyrifos is teratogenic and embryotoxic in rats even at low doses of contamination. In this context, the adsorption process using biomass becomes an excellent alternative for removal of these molecules, especially when using modified residual biomass, which have higher pollutant removal capacity when compared to biomass in nature. This way, the current research produced modified adsorbents with solutions of H₂O₂, H₂SO₄ and NaOH 0.1 mol L⁻¹ and cassava barks. The relationship between pH of chlorpyrifos solution, adsorbent masses and removal capacity was evaluated. In Figure 1 are presented the results of adsorption tests for chlorpyrifos removal from water by modified and natural adsorbents of cassava.

Figure 1. Response surfaces for removal of chlorpyrifos according to adsorbents masses of cassava and pH of the solution.

The modified adsorbents of cassava presented highly absorptive capacity for chlorpyrifos removal, especially the modified adsorbent M. NaOH, which presented increase of 60% in the removal capacity. It highlights the non dependence of evaluated pH range, which presented a great result, indicating that these modified and natural adsorbent can be used in many pH conditions, without loosing its effectiveness in adsorption of chlorpyrifos.

Acknowledgement - The authors would like to thank the CNPq for its funding and research productivity and the CAPES for the postgraduate scholarship.
Transport of *E.coli* in saturated porous media - Effect of humic acid

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Different kinds of colloids co-occur in natural environments. Colloids, like natural organic matter, clay particles and nanoparticles co-present in solutions, could have marked outcome on the transport of bacteria (Yang et al., 2016). Natural organic matter, made up of organic substances originating from plants and animals is ubiquitously present in environment. The organic content includes lipids, proteins, humic substances, hydrophilic acids and amino acids. These substances have redox active functional groups that interacts with bacteria present in natural environment (Yang et al., 2012). Of them humic substances appear most abundantly and hence requires an understanding of its effect on the transport of bacteria. Saturated column studies were performed to study the effect of humic acid on the transport of bacteria. The breakthrough curves of the transport of bacteria with humic acid augmented cell transport. Further column studies were conducted to understand the possible processes. Transport of humic acid alone was examined in saturated column experiment and it showed that there was no retardation but some deposition of humic acid was evident from the C/C₀ value of 0.95. Also, the transport study was conducted with pre-treating the column with humic acid first and then passing the bacteria through the saturated column. It was found that the breakthrough of bacteria was higher for media with pre-treatment than in the media without pre-treatment. And it was lower than the media without pre-treatment and with humic acid. Earlier research has reported that site competition and deposition by suspended humic acid could contribute to the enhanced bacterial transport (Yang et al., 2012). However, the experiment on transport of humic acid alone shows that in addition to these two mechanisms, straining could be the phenomenal mechanism that is responsible for this behaviour as evident from the column experiments. And the presence of humic acid could affect the distribution of microbes in the subsurface leading to contamination issues.

References
Assessing the transport of iron oxide nanoparticles in a large-scale 3D model aquifer

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In the framework of the research project NanoRem (FP7 - G. A. Nr. 309517) the possibility of using iron oxide nanoparticles (FeOxNPs) in remediation of real field sites by characterizing the transport of FeOxNPs in a large-scale three-dimensional (3D) model aquifer was investigated. Therefore, different complementary methods for detection, quantification and transport characterization of FeOxNPs were evaluated.

Batch-scale experiments were performed in order to elucidate the potential of the complementary methods for direct and indirect characterization and detection of FeOxNPs. Direct methods included measurements of particle size distribution, particle concentration, Fe$_{tot}$ content and turbidity of the FeOxNPs suspension. Indirect methods included measurements of particle zeta potential, as well as TOC content and pH of the FeOxNp suspension. The results of the batch experiments indicated that the most suitable approach for detecting and quantifying FeOxNPs was measuring Fe$_{tot}$ content and suspension turbidity, as well as particle size determined using dynamic light scattering principle.

Best performing complementary detection methods were further applied in a 3D large-scale study containing medium and coarse sand in order to 1) assess the transport of FeOxNPs in saturated porous medium during injection ($V_{FeOx} = 6\ m^3$, $c_{particle} = 20\ g/L$, $Q_{inj} = 0.7\ m^3/h$), and 2) illustrate their spatial distribution after the injection. Monitoring data including Fe$_{tot}$ content, turbidity and particle size revealed the transport of particles towards to high permeability zone creating a radius of influence of 2 m. Finally, the results of the large-scale 3D study have shown that delivering of the FeOxNPs to the contaminant zone is feasible.
Interfaces Against Pollution
Environmental Challenges & Opportunities

Agar agar improves stability and mobility of milled ZVI used in groundwater remediation

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Submicron-scale milled zerovalent iron (milled ZVI) particles produced by grinding macroscopic raw material could provide a cost-effective alternative to nano-scale zerovalent iron particles for in situ groundwater remediation. Application of particles for in situ remediation requires optimal particle delivery to the contaminated zone, which is influenced both by the injection technique and the mobility of the particles in the subsurface.

Milled ZVI has shape of a flake with a lateral size of several micrometers and a thickness of less than 100 nm (Figure 1). Bare milled ZVI particles aggregate fast in aqueous suspension and remain immobile in the subsurface [1]. In order to improve mobility of milled ZVI particles in the subsurface, an optimal stabilization of the particle suspension was required.

Figure 1: SEM image of milled ZVI (source: UVR-FIA GmbH)

Potential of different polymers (agar agar, carboxymethyl cellulose, guar gum, starch and lignin sulfonate) to increase the stability of milled ZVI suspension was firstly tested. Based on the outcomes of a detailed characterization of such modified suspensions in terms of particle size, zeta potential, particle sedimentation rate and suspension viscosity, agar agar was selected as the most efficient stabilizer.

Mobility of agar agar-stabilized milled ZVI suspension was then tested in flow-through columns packed with porous media with different texture and mineralogical composition. Agar agar-stabilized suspension of milled ZVI showed a considerably higher mobility potential compared to that of pure aqueous suspensions where no breakthrough was observed. Particle breakthrough in the stabilized suspension varied between 0.84 and 0.97. The particle breakthrough observed for various porous media depended on the sediment texture, while the geochemical heterogeneity within the sediments had only a minor impact.

References

Acknowledgement
This research was conducted within the framework of the European Union NanoRem project (FP7 - Grant Agreement Nr. 309517).
Composition and characteristic of natural inorganic nanoparticles in Chinese soils

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Natural inorganic nanoparticles are widespread in soils but their composition and properties have not been studied widely. We used centrifugal process and an automated ultrafiltration device (AUD) to extract coarse particles (450-2000 nm) and nanoparticles (25-100 nm) from 4 soils (Alf-1, Alf-2, Ult-1 and Ult-2) sampled in different regions of China. Various techniques were used to study the composition and characteristics of the two size particles, including zeta potential, IEP (isoelectric point), conventional and synchrotron X-ray diffraction (XRD) analysis. The results showed that the nanoparticles had higher zeta potential and IEP than the coarse particles. And the IEP of Alf-1 and Alf-2 nanoparticles were below 2.0, Ult-1 and Ult-2 nanoparticles were 3.27 and 4.37, respectively. The content of free Fe and Al (Fed and Ald) and crystalline Fe-oxides was observed to achieve maximum in nanoparticles. The crystalline Fe-oxides were hematite and goethite that were identified by powder XRD patterns. Additionally, the natural inorganic nanoparticles existed amount of phyllosilicate minerals, which mainly were kaolinite and illite. With particles size decreasing, the clay mineral structures were transformed from well crystalline to poor crystalline. The hydroxyl groups between the tetrahedral and octahedral structures of the 2:1 clay minerals and the surface of kaolinite gradually broke down. The analysis of kaolinite crystallization parameters in Ult-1 and Ult-2 showed that the reduction of the mean crystal dimension (MCD) and average layer numbers (ALN) of kaolinite by about 50 Å and 6 layer unit cells, Hughes and Brown (H&B) index by 5-10.4 in nanoparticles than 450-2000 nm particles. Characteristics of nanoparticles provide useful information for further research on adsorption of elements and environmental pollutants by soil nanoparticles.

Acknowledgement - The authors thank beamline BL14B1 (Shanghai Synchrotron Radiation Facility) for providing the beam time. This research was supported by the National Natural Science Foundation of People’s Republic of China (Grant No. 41271252), and the Fundamental Research Funds for the Central Universities (2013PY002).
PEST-ORCHESTRA: A tool for optimizing NICA-Donnan model parameters for humic substances reactivity

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Humic substances are a complex mixture of macromolecules that have a high affinity for metal ions and can affect their mobility and bioavailability in the environment. Due to the high heterogeneity of humic substances, their reactivity is difficult to determine, and several models exist to describe their acid-base properties and their complexation to metal ions. Among the various speciation model platforms, the software ORCHESTRA [1] has the advantages to be independent of the operating system and free. Furthermore, it is very flexible, since its model definitions are in text format and thereby accessible and can be modified by users for extensions and modifications. However, until now, no method is available to optimize model parameters using ORCHESTRA. Here we describe the coupling of the PEST parameter optimization software (http://pesthomepage.org/) with the ORCHESTRA speciation software, and validate this method as a way to describe humic substances reactivity within the framework of the NICA-Donnan model [2], by comparing our results with literature data.

The optimization procedure has been applied to obtain optimum NICA-Donnan parameters for the binding of protons and metal ions to Laurentian fulvic acid (LFA). An unconstrained fit gave us proton-binding parameters in good agreement with the results obtained by Milne et al. [3] on the same dataset using the FIT software. This allows us to validate our approach. A more constrained procedure to determine proton-binding parameters for LFA is also proposed, adapted from Lenoir et al. [4].

Furthermore, this method is applied to optimization of Pb-binding parameters for the same LFA. PEST-ORCHESTRA optimization gives results that are of the same order of magnitude than the ones obtained by Milne et al. [5] if input parameters are identical (generic fulvic acid proton-binding parameters). However, the optimization procedure yields significantly different values when LFA-specific proton-binding parameters are used as input: logK⁹⁰⁺,Pb increases from -0.98 to -0.47 and logK⁺,Pb from 6.55 to -0.43, even if the calculated amounts of LFA-bound Pb are comparable in both cases. This procedure is also applied to derive parameters for Cd- and Zn binding to LFA, which were lacking till date.

References
Dynamics of benzo(a)pyrene in porous media of sediments and soils

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Hydrophobic organic compounds (HOC) are often associated with sediments and soils (S&S) in contaminated areas. HOC include aromatic compounds from petroleum and fuel residues, chlorinated compounds from commercial solvents and other chemicals. HOC adsorbed in S&S may signify risks to ecosystems and human health since these contaminants are often released over time from the porous matrixes of S&S to interstitial and surrounding water when HOC are exchanged between sorbed and dissolved phases. In this manner, S&S may act as secondary pollution sources long after traditional remediation actions of these porous media have terminated. The physical and chemical characteristics of S&S and their interaction with the HOC would control such accumulation and release. For HOC, sorption, desorption and diffusion are critical processes controlling the fate of these chemicals in aqueous systems. Bioavailability of HOC is affected by these processes in two important ways. First, sorption is expected to cause relatively higher accumulations of HOC in micropores (< 6 nm) due to the larger surface areas in these openings that are so small that biodegrading bacteria (with radii typically > 200 nm) have no access. Second, because desorption and diffusion must occur before biodegradation can proceed. Therefore, the overall rate of bioremediation can be limited or even controlled by such chemical and mass transfer processes, and not only by the activity of the degrading microorganism. It is important to understand and be able to predict the transport and fate of HOC for choosing effective remediation procedures. The pore size distribution is known to be one of the main factors that determine the sorption/diffusion processes in S&S.

Samples of S&S were characterized for their particle size distribution, surface area and pore size distribution, mineralogy, and organic carbon content. Nitrogen gas adsorption and the BET isotherm were used to characterize the porous nature and the specific surface area of the S&S samples. A BET surface area and pore size distribution analyser model Autosorb IQ² (Quantachrome) was employed on previously degassed samples. Benzo(a)pyrene (BaP) was chosen to carry out sorption, desorption and diffusion experiments in the S&S with different pore size distributions. In split samples, organic matter was eliminated by adding dilute hydrogen peroxide. The organic matter content was estimated as the weight difference before and after the hydrogen peroxide digestion, and compared to the organic matter content determined by calcination. Experimentally obtained kinetic and equilibrium coefficients were related to the pore distributions of S&S. Experiments were performed using 7-¹⁴C-BaP and an isotopic dilution technique, where the tracer activities in the supernatant and solid-phase extracts were quantified for time-dependent measurements, in a liquid scintillation counter (Beckman Coulter LS 6500). Sorption kinetics were determined for 7-¹⁴C-BaP in S&S porous media with limited microbial activity. To evaluate the effect of diffusion in pores, mass balances of BaP were performed for each experiment. Analyzing results of experiments with different relations BaP/S&S, the sorption equilibrium constants of BaP in the different samples of S&S were obtained, and the Koc distribution coefficients of BaP in S&S organic carbon were determined. A kinetic model was applied to distinguish diffusion in pores from the process of sorption inside the pores.

Based on the generated knowledge, we developed a conceptual model that describes the effect of the dynamics in porous media on the reactive transport of BaP in S&S with different pore size distributions.
Strength development and durability of non-OPC geopolymer mortar for Low CO₂ emission

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Abstract

One of the major challenges facing mankind since the start of the 21st Century is not only the ever deteriorating climatic conditions but the unpredictability of the weather as well. One of the industrial activities by mankind that lead to the increase in the carbon dioxide in the atmosphere is the manufacture of Ordinary Portland cement (OPC), a common binder in the construction and civil engineering industry. Carbon dioxide emissions from OPC production is about 7% of the total carbon dioxide emissions.

And then, for low CO₂ emission binder as OPC, We investigated the strength development and durability of geopolymer mortar using blast furnace slag only, and admixed with blast-furnace slag and fly ash as cementitious materials in order to develop none-OPC geopolymer mortar (NOGM) for low CO₂ emission binder. For improving of early compressive strength of NOGM, we used calcium aluminate compounds (CAC). Calcium aluminate compounds (CAC) clinker developed by sintering industrial waste and by-products with much CaO and Al₂O₃ and sulfate. In order to compare with the geopolymer mortar, the normal mortar using Ordinary Portland Cement (OPC) was also test. In view of the results, we found out that early strength development, the resistance to freezing-thawing of the NOGM have better than the mortar using Ordinary Portland Cement (OPC).

References

Non-linear accumulations in Diffusive Gradients in Thin films (DGT) devices: competition, saturation and kinetic effects.

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DGT (Diffusive Gradients in Thin films) was designed to sample trace metals in situ at their natural concentrations. The set-up and the experimental deployment conditions were established to allow interpretation of a linear metal accumulation with time using a simple expression based on a steady-state flux under perfect sink conditions [1]. However, the extension of DGT to a wide range of analytes and its use in varied conditions (from soils and sediments to fresh and marine waters) has shown that, in some situations, these conditions are not fulfilled [2-3], so that accumulations with time may also be non-linear. This contribution systematically and quantitatively considers how non-ideal accumulation can occur. It presents a set of expressions to interpret the DGT accumulations in simple systems when there are: i) kinetic limitations in the binding to the resin, ii) saturation or equilibrium effects, or iii) non-negligible competitive effects. The binding of Mg or Mn cations are used to exemplify the use of these expressions. Concentrations calculated therein show reasonable agreement with the experimental values and with the results of a numerical model of the dynamic DGT – solution system, significantly improving the estimations based on perfect sink conditions. The outcomes of the work are related to published examples of non—ideal accumulations [4].

References

Acknowledgement - Financial support from FEDER and the Spanish Ministry of Education and Science (Projects CTM2012-39183 and CTM2013-48967) is gratefully acknowledged.
Elaboration by hydrolysis in polyol, Characterization, Adsorption and anionic exchange properties of a new Co-Fe-Acetate nanohybrid for Direct red 2 as a model anionic dye

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Abstract
In recent years, many studies have been devoted to investigating the ability of LDHs to remove harmful anions such as colored textile dyes from wastewaters [1]

In the present study, pure Co-Fe-Ac layered double hydroxide (LDH) intercalated by acetate anions with a Co / Fe molar ratio of 3.0 was prepared by hydrolysis in polyol medium under moderate thermal treatment, and have been employed to remove an anionic dye (direct red 2) from aqueous solution.

Co-Fe-Ac XRD and FTIR spectroscopy patterns show a structural feature characteristic of hybrid LDH, and the interlayer distance of 12.70Å confirms the intercalation of acetate anions into the structure [2].

In order to check the capacity of our material to exchange the acetate anions inserted in its interlamellar space, anionic exchange in aqueous medium with CO₃²⁻ anions was realized for this compound. The as-obtained compound CoFe- Ac /EC (exchanged) has an interlamellar distance d₀₀₃ = 7.67Å which corresponds perfectly to the presence of the carbonate anions and the water molecules in the interlayer space.

The adsorption of direct red 2 by Co-Fe-Ac LDH has been examined in order to measure the capability of this new organic/inorganic nanomaterial to eliminate this highly toxic azoic class of anionic dyes from wastewater and was compared with that of CoFe- Ac /EC. The quantity of dye eliminated was found to depend on contact time, pH, initial concentration of dye and heating temperature.

The adsorption isotherm displays the typical L shape according to Giles’s classification [3], where its saturated adsorption capacity is 596.83 mg/g. The suitability of the kinetic and isotherm models for this adsorption was also discussed, and the results showed a good compliance with the Langmuir, Redlich-Peterson, Toth isotherms and the pseudo-second-order kinetic model.

The thermodynamic parameters ΔG°, ΔH° and ΔS° were calculated to predict the nature of adsorption and results suggested that this reaction was a spontaneous, endothermic and chemical process. Where the localization of the dye in the interlayer space and/or on external surfaces of the nanomaterial was studied by X-ray diffraction (XRD), as well as by infrared spectroscopy (IR).

Taking account of these results, and comparing them with those already obtained for a material known by his great power adsorbent MgAl-500 (hydrotalcite synthesized in aqueous medium and calcined at 500°C) [4], we can conclude that prepared LDHs by forced hydrolysis in a polyol medium can be used successfully in the removal of anionic dyes from aqueous solutions (Until 2g/l of dye solution concentration with a removal efficiency of 100%).

Effects of (doped) rare earth oxides on algae, bacteria, protozoa and crustaceans

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Rare earth oxides (REO) are increasingly used in e.g., catalysis, electronics and as fuel additives. Some RE elements (REE) such as gadolinium are also used in health-related applications. In general, REE are considered of average supply risk, low environmental implications and low-to-medium vulnerability to supply restrictions [1]. However, REO are exerting toxic effects via different mechanisms than oxides of non-rare earth metals, at least in the acidic environment of cellular lysosomes [2]. By taking on board our extensive experience in (eco)toxicity studies of nano and bulk metal oxides [3] we evaluated the biological effects of CeO₂, LaCoO₃, LaFeO₃, LaNiO₃, Gd- and Pr-doped CeO₂, Gd cobalt oxide, Sr-doped LaMnO₃ and Sr-doped LaCoO₃ to species on different food-web level. The REO were synthesised by CerPoTech AS (Norway). Most of the primary particles of REO were in the range 50–500 nm. To evaluate the adverse effects due to shedding of the metal ions, soluble salts of all chemical elements included in the materials were studied in parallel. Potential of REO to create reactive oxygen species in vitro was evaluated using two different fluorescent dyes, H2DCF and HPF. As a rule, highest concentration of REO tested for toxicity was 100 mg/L.

CeO₂ and Gd-doped CeO₂ showed some toxic effects to crustaceans Thamnocephalus platyrus at the concentration range 10–100 mg/L, probably due to shed Ce-ions. The rest of the studied REO were not toxic to crustaceans (24h EC50 values > 100 mg/L). No toxic effects to protozoa Tetrahymena thermophila (24 h EC50>100 mg/L) as well as to bacteria Vibrio fischeri (30-min EC50 >500 mg/L) were observed.

The studied soluble salts were remarkably more toxic: La, Ce and Gd were toxic (i.e. EC50<100 mg/L) in all five bioassays (bacteria Escherichia coli and V. fischeri, crustaceans T. platyurus, protozoa T. thermophila, algae Pseudokirchneriella subcapitata), Co was toxic in three tests and Mn and Ni in two tests. Sr was not toxic (EC50>100 mg/L) in any bioassay used. The most sensitive assay was algal growth inhibition test and most toxic to algae were Co and Ni (EC50<1 mg/L).

Assumingly, CeO₂ and Gd-doped CeO₂ were toxic to crustaceans due to leached Ce ions. Although some of the oxides (LaNiO₃, Sr-doped LaCoO₃ and Sr-doped LaMnO₃) were producing remarkable amount of reactive oxygen species in vitro, no obvious correlation with the toxicity was found. The evaluation of toxicity of REO to algae is in course.

References


Acknowledgement - This research is supported by Estonian Ministry of Education and Research (target-financed theme IUT23-5 and PUT748)
Leaf stoichiometry of three tree species grown in different soils and exposed to elevated ozone concentration

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Ground level ozone (O₃), whose levels are increasing in Asia, is vigor and health of plants [1]. Previously, we investigated foliar starch and sugar contents and stoichiometry of leaves of 2-year-old seedlings of two oak species (Quercus serrata and Q. mongolica var. crispula) grown under elevated O₃ and CO₂ in a free-air enrichment system. We found that N and Mg could be major indices in assessing the O₃ effects on these species [2]. Retranslocation, one of the most important functions in perennial plants, can be assessed by the amount of an element depleted from old plant components and transferred to newer components. Leaf senescence is usually accelerated at elevated O₃ doses (eO₃) and influenced by soil nutrient availability (and acidification). Hence, we conducted another experiment to assess eO₃ effects on nutrient retranslocation across three tree species native to northern Japan (Betula platyphylla var. japonica: white birch, Q. mongolica var. crispula: oak, and Fagus crenata: Siebold’s beech) in relation to different soil conditions. In this study, we focused on the effects of eO₃ on the retranslocation of 8 essential foliar elements (N, P, Mg, K, Ca, Mn, Fe and Al).

We planted 3-year-old seedlings of the three species in a free-air O₃ enrichment system with three soil types (brown forest soil, serpentine soil and volcanic ash soil) for one growth season. The seedlings were grown in three plot replicates per ozone treatment: eO₃ (targeted 70 nmol mol⁻¹) and ambient (ranging 25-35 nmol mol⁻¹). Upper and shed leaves were collected (mid-September and mid-November, respectively) for chemical composition analysis. In birch, retranslocation rate of P was markedly increased by eO₃. Foliar nutrient retranslocation of oak was affected by the interaction of ozone and soil treatments. Beech was more responsive, regarding retranslocation, to eO₃ and soils than birch and oak species. We conclude that beech, a species with determinate growth, can be an index species for investigating the mineral nutrients retranslocation system in field surveys.

References

Acknowledgement This study is supported in part by Grant-in-Aid for challenging exploratory research (16K14932) and Type B (26202975) to T.K.
Phosphate adsorption on kaolinite and its effect on the kaolinite stability at various solution conditions

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1. Introduction
Phosphate, which is applied to crop fields as a fertilizer, is chemically strongly adsorbed on the clay minerals in soils. Phosphate adsorption affects the colloidal stability of clay because it changes the surface charge of the clay. Dispersed clay particles with adsorbed phosphate will be conveyed by water movement and when phosphate is discharged into the aqueous environment eutrophication may occur. Therefore, understanding phosphate adsorption and clay stability are important concerning effective phosphate application, colloid leaching and environmental preservation.

In this study we examined how the phosphate adsorption to kaolinite and the kaolinite stability changed with pH and electrolyte concentration. Kaolinite is a 1:1 clay that has not only a permanent negative plate charge, but also a substantial variable edge charge.

2. Materials and Methods
The kaolinite particles with diameter <2 μm, obtained by sedimentation, were used. The phosphate adsorption experiments were conducted by batch method at a prescribed pH (pH 3, 4, 5, 6, 7) and NaCl concentration (1 or 10 mM); NaH2PO4 solutions were used as phosphate source. After equilibration for 24 hours the phosphate (P) concentration was measured by the ascorbic acid method, as well as the Na and Cl concentrations and the amounts of adsorbed P, Na and Cl were calculated. The electrophoretic mobility of clay particles was measured with the microelectrophoresis method and the flocculation rate by the dynamic-light-scattering method at the same solution conditions as the adsorption measurements. The zeta potential was estimated from the mobility using Smoluchowski’s equation. From the flocculation rates the stability ratio was calculated. The interaction potential energies of the kaolinite particles were calculated from zeta potential by using the DLVO theory and assuming that the particles were simple spheres with a homogeneous surface charge density.

3. Results
Phosphate adsorption and zeta potentials. The pH and electrolyte concentration determined the amount of adsorbed phosphate; the maximum phosphate adsorption was observed at pH 6 at both NaCl concentrations. Under all experimental conditions, zeta potentials were negative and in the range -56.4 mV to -11.3 mV. The zeta potentials became more negative with increasing pH and phosphate sorption. By modeling the kaolinite surface charge with a multi-site type model (CD-MUSIC), these characteristics could be reproduced qualitatively.

Stability of kaolinite. At pH 3 and 4, the kaolinite flocculated irrespective of the NaCl concentration and the adsorbed amount of phosphate. At pH 5 to 7 and 1 mM NaCl and at pH 6 to 7, and 10 mM NaCl, the stability ratios increased with phosphate adsorption. The dispersion stability corresponded with the decrease of the zeta potential (increasingly negative). Kaolinite became well dispersed if the zeta potentials were lower than about -40 mV. For this potential the DLVO maximum interaction potential energy was about 500 k_BT, (k_B Boltzmann constant; T the absolute temperature). This value is much larger than the common 15~20 k_BT for classical colloidal particles. The difference is likely due to the complex surface charge characteristics of kaolinite.
Tylosin removal in an aqueous suspension by photocatalysis at 254 nm

Laoufi' N. A., Nezar' S., Dechir' S., Akkar' M., Mouheb' A.


Antibiotics are considered as emerging environmental microcontaminants because of their potential adverse effects on ecosystems and human health. Photocatalysis, in presence of TiO₂ particles, is one of the most promising techniques for the removal of antibiotics. In the present work, photodegradation of tylosin, a veterinary antibiotic, has been released in a double-spiral photoreactor containing a suspension of a Degussa P25 TiO₂ catalyst under 18W, with a 254 nm low pressure mercury lamp irradiation which is set in axial position in the open space of the sheath. Different parameters were investigated on the removal of tylosin, as concentration of antibiotic and catalyst, pH, flowrate, effect of different acids and bases, effect of H₂O₂ and effect of different catalysts (DT51, EL10, PC105, P25 and PC 500, T42) and optimized values were obtained. Results showed that removal efficiency was increased by the decreasing amount, the oxidation was complete after an irradiation time of 4 hours at low concentration (10 mg/L and less), rejection also increased at low pH (3 and 5 unadjusted and adjusted along the photodegradation), where, most of tylosin was oxidized. It is also evident that the photodegradation percentage increased with increasing irradiation time. Furthermore, we noted that an increase in the initial concentration of catalyst (0.005 to 1 g/L) did not give a significant improvement in the level of removal, thus, 100% of tylosine has been oxidized after an irradiation time of 4 hours, however, the oxidation rate was fast with high concentrations. Experimental studies showed that the best acid for tylosine photodegradation was H₃PO₄ and all bases and H₂O₂ disadvantaged the process.

Even though diazinon was slightly adsorbed on P25, the best degradation was observed with this photocatalyst, contrary to PC 105 which appeared the best adsorbent (45% of tylosine were adsorbed), but showed a tylosin reduction of 50% after an irradiation time of 3 hours. The rate constants for the different parameters were evaluated. The kinetics was described by the Langmuir-Hinshelwood kinetic model. An overall pseudo-first order kinetic constant has been calculated for tylosin conversion.
Photocatalytic oxidation of a pharmaceutical pollutant in aqueous suspension of zinc oxide

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In the context of wastewater treatment plants, new methods of treatment have been developed. These techniques allow the total mineralization of non-biodegradable organic pollutants, heterogeneous photocatalysis processes (AOPs) is one of these AOPs. The objective of the present work is based on the degradation of a painkiller “acetaminophen” or paracetamol in a screw reactor in presence of a catalyst ZnO suspension under UV irradiation. The UV lamp (HPA 18 W/S with a monochromatic radiation at 365 nm and a nominal power of 18 W), is set in axial position in the open space of the sheath. The influence of parameters as initial flowrate, catalyst and pollutant dose, solution pH, different type of catalysts and the wavelength emitted by UV lamp have been studied in order to optimize operational conditions of the photodegradation process. The experimental results showed that the photodegradation of paracetamol increased significantly compared to adsorption and photolysis. The parametric study of the pollutant oxidation showed that the degradation depended on the different parameters. Furthermore, we noted that an increase in the initial concentration of paracetamol disadvantaged the reaction, and an increase in the initial concentration of catalyst (0.05 to 0.2 g/L) advantaged the oxidation of paracetamol, abatement of acetaminophen was complete after 5 hours of radiation exposure with 0.2 g/L of ZnO. Results showed that 98% of paracetamol were oxidized after 5 hours radiation exposure with an optimum flowrate of 195 mL/min. Results showed also that the presence of acids or bases disadvantaged the process, so, it is better to study the photodegradation of paracetamol at free pH, where we observed an increase of pH during the oxidation, indicating the formation of inorganic and organic bases which caused the rise of pH solution, in this case, 93% of paracetamol was oxidized. Photodegradation of paracetamol oxidation is first order reaction and the model of Langmuir-Hinshelwood was employed to describe this kinetic. Wavelengths emitted by UV lamp (254 nm and 365 nm) with same power (18 Watts), indicated that paracetamol was significantly eliminated at 365 nm where79% have been oxidized, whereas this percentage does not exceed 20% at 254nm.

Photodegradation of paracetamol in presence of ZnO and TiO$_2$ with different ratios showed that paracetamol oxidation was highly favored by titanium dioxide, where 99% has been destructed.
Adsorption of toxic and potentially toxic ions by wheat straw in simple system

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The aim of this study was to verify the wheat straw adsorption capacity, alone, subjected to different concentrations of F, Cd, Pb, Cr(VI), Cu, Ni and thus decrease the mobility and availability of these elements in soils after fires or mining, reducing risks of soil and water contamination. For the adsorption studies was added 3.0 g of adsorbent and 30 ml of NaNO₃ (0.01 M) solution with increasing concentrations (0, 0.5, 1.5, 3.0 and 6.0 mmol L⁻¹) of Cd, Pb, Cu, Ni, F and Cr(VI). The samples were shaken for 24 hours, filtered and determined the pH of the solution after adsorption, dissolved organic carbon (DOC) and the equilibrium concentration of the elements. For desorption, in each filtered sample of adsorption experiments were added 30 ml of NaNO₃ (0.01 M), and stirred for 24 hours. Was tested the competition of Pb, Cd and Cu on adsorption of wheat straw were studied (Figure 1). Then the % adsorption isotherms were calculated and the models of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) were applied (Table 1).

Figure 1. Cation adsorption percentage [Pb, Cd, Ni, and Cu] and anions [Cr(VI) and F] from wheat straw according to the initial concentration (C₀: 0, 0.5, 1.5, 3.0 and 6.0 mmol L⁻¹).

Table 6. Parameters of mathematical models Langmuir, Freundlich and Dubinin-Radushkevich (DR) related to the cation adsorption [Pb, Cd, Ni, and Cu] and anions [Cr (VI) and F] by wheat straw

<table>
<thead>
<tr>
<th></th>
<th>Constants of Langmuir</th>
<th></th>
<th>Constants of Freundlich</th>
<th></th>
<th>Constants of D-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qm</td>
<td>(mmol kg⁻¹)</td>
<td>b ou K</td>
<td>Rᵢ</td>
<td>R²</td>
<td>Kₑ (mmol kg⁻¹)</td>
</tr>
<tr>
<td>F</td>
<td>117.803 e³</td>
<td>2.280 e⁴</td>
<td>0.956</td>
<td>0.966</td>
<td>25.339</td>
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<tr>
<td>Pb</td>
<td>339.456 e³</td>
<td>5.290 e⁴</td>
<td>0.904</td>
<td>0.762</td>
<td>879.346</td>
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<tr>
<td>Cd</td>
<td>76.712</td>
<td>1.569</td>
<td>0.003</td>
<td>0.997</td>
<td>52.011</td>
</tr>
<tr>
<td>Ni</td>
<td>736.326 e³</td>
<td>2.690 e⁶</td>
<td>0.985</td>
<td>0.978</td>
<td>18.176</td>
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<tr>
<td>Cu</td>
<td>156.649 e⁶</td>
<td>2.490 e⁶</td>
<td>0.995</td>
<td>0.856</td>
<td>40.946</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>129.029</td>
<td>3.273 e²</td>
<td>0.133</td>
<td>0.948</td>
<td>4.342</td>
</tr>
</tbody>
</table>

Qₑ: maximum capacity of adsorption; b or Kₑ: constant related with the forces of interaction between adsorbent/adsorbate; Kᵢ: constant of Langmuir; Rᵢ: coefficient of determination; Kₑ: related with the capacity of adsorption; n: related with heterogeneity of the solid; Qₑ: maximum capacity of adsorption; E: medium energy of sorption.

Were observed good mathematical fittings to Langmuir model for the removal of F, Cd, Ni, and Cu, D-R for the adsorption of Cu and Cr(IV), and the model of Freundlich with good fittings for all elements evaluated. Pb and Cd obtained high rates of adsorption and low desorption rate (%). The Cu, F and Ni even with low adsorption rate (%) were obtained low desorption rate (%). The Freundlich model best explains the adsorption for all the studied ions, primarily for Ni, Pb and F, suggesting the occurrence of multilayer adsorption. The results show that the use of wheat straw as adsorbent in natura on remediation of contaminated water with metals is an excellent alternative, depending on the removal rates, nature of the adsorption process and low operational costs.

Acknowledgement - The authors would like to thank the CNPq for its funding and research productivity, the CAPES for the postgraduate scholarship and to the University of Santiago de Compostela for the scientific international cooperation.
Anthropogenic aluminium scavenging in marine sediment

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Natural marine sediment (SL) was collected on a weakly urbanized zone situated in the North-West of France. Al total concentration (28±1 g.Kg⁻¹) was determined by ICP-AES following sample dissolution using alkaline fusion. To estimate the Al-mobility, a sequential extraction (Leleyter et al. 1999) was performed. This procedure selectively and efficiently dissolves all the chemical constituents of the sediments (water soluble F1, exchangeable F2, acido-soluble F3, reducible F4 and oxidable F5 fractions). F6 is the sum of all these labile fractions. The leachable part of the natural Al (2.6±0.1 g.Kg⁻¹) is almost exclusively found in the reducible fraction (95 %) with only 5% in the oxidable fraction (see figure 1). 3 different contamination tests were then realized. SL was contaminated by 2 aluminium salts (aluminum sulfate or chloride, resulting samples noted SL_sulfate or SL_chloride) and by aluminium sacrificial anode (contaminated sediment noted SL_anode).

Aluminium contamination tests (by salts or sacrificial anode) induce an increase of Al total concentration with regard to the initial aluminium SL concentration (Al concentration is equal to 29 g.kg⁻¹ in SL_anode and to 33 g.kg⁻¹ in salts contaminated sediments). Concerning the aluminium total content, we note here no difference induced by the salt nature (sulphate or chloride). However a strong increase of Al mobility is noticed: F6-leachable percentage is equal to 9±1%, 11±1% and 18±2% respectively in SL, SL_chloride and SL_sulfate. This increase of the Al-lability is even more pronounced for the sample contaminated by sacrificial anode (F6-leachable percentage equal to 32±1% in SL_anode). This increase of Al-lability could be explained by the speciation of labile aluminium (see figure 1) which is mainly bound to the reducible fraction (> 94 %) in the salts contaminated sediments, whereas the labile aluminium is bound to the acido-soluble and oxidable fractions (31%) for the sediment contaminated by sacrificial anode. An increase in Al bound to the acid-soluble fraction was also observed in sediments close to the Al anodes (Gabelle et al. 2012).

The nature of the contamination (aluminium salts or aluminium sacrificial anode) impacts on the mineralogical fraction concerned by Al-scavenging.

References :
Oxalate influences the environmental fate of ferrihydrite colloids via dissolution mechanism

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The dissolution of iron hydroxides induced by LMW organic acids has been proposed as one of the important mechanisms for colloid generation and removal. However, relatively limited studies have explicitly investigated what roles the different surface complex species play in the process of generation and removal of the colloidal particles under a disturbed environment. The aim of studying desorption characteristics of oxalate from ferrihydrite and effect on ferrihydrite dissolution is to help to fully elucidate fate and transport mechanisms of colloids and pollutants in the environment.

ATR-FTIR and two-dimensional correlation spectroscopy showed that there are inner- and outer-sphere complex of oxalate simultaneously on surface of ferrihydrite and the two species are dependent on each other. Oxalate solution concentration has strong influence on desorption rate of oxalate surface complex. Regression analysis of the desorption data indicated desorption rate constants of two complex species at high oxalate surface coverage is larger than ones at lower surface coverage. The mathematical modeling of ferrihydrite dissolution and colloid stabilization kinetics and column flow-through experiments suggest the stabilization of ferrihydrite colloids dominated over dissolution into dissolved Fe at oxalate lower surface coverage, driven by electrostatic repulsive forces from the unsaturated strongly-bound species. Outer-sphere complexes, at high oxalate surface coverage, induced the dissolution of aggregates and colloids of ferrihydrite into dissolved Fe. Our results provide insights into the fate of iron hydroxides colloids in soils and aquatic environments.

Figure 1: The process of ferrihydrite dissolution and colloid stabilization under the influence of the different coordination modes of surface complex.

Acknowledgement - The authors thank the Natural Science Foundation of China (Grant Nos. 41330852 and 41425006) and the National Key Basic Research Program of China (No. 2015CB150504) for the financially support.
Adsorption of Sodium Dodecylsulfate and Dodecylpyridinium Chloride on Silica

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Introduction: Anionic surfactant sodium dodecylsulfate (SDS) adsorption on silica was systematically investigated at different pH (3, 4.5, 5 and 7) and NaCl concentration (0.1, 1, 10, and 100 mmol/L). Cationic surfactant dodecylpyridinium chloride (DPC) adsorption on silica was studied at pH 5 and 10 mmol/L NaCl. The conditional maximum adsorption was obtained with the Langmuir equation.

Materials and Methods: Silica was purchased from Sigma-Aldrich with a purity of 99.5%. The specific surface area was 414 m²/g, the mean particle diameter 1.2 μm and the average pore diameter 7 nm. The surface charge density of silica samples at different electrolyte concentrations was measured by acid base titration at 25 ± 1°C. SDS with purity of 99.0% and DPC with purity of >98% were purchased and used without further purification. A batch method was used to obtain the adsorbed amount of the surfactant. The equilibrium concentration SDS was measured with an anionic surfactant selective membrane electrode and that of DPC was measured by UV-absorbance at 255 nm. Zeta potential of the silica particles were obtained by measuring the electrophoretic mobility and calculated with Smoluchowski equation.

Results and Discussion: SDS. At 0.1 mmol/L NaCl solution no SDS adsorption was observed, the electrostatic repulsion between the surfactant and the silica was too strong. However, at NaCl concentrations ≥ 1 mmol/L the repulsion was sufficiently reduced and SDS adsorbed through hydrophobic attraction. At NaCl concentrations ≥ 1 mmol/L, SDS adsorption increased with decreasing pH because of the decreasing electrostatic repulsion. For pure silica the decrease of the repulsive electrostatic potential with increasing NaCl concentration and decreasing pH were confirmed by the measured zeta potential and surface charge density.

DPC. DPC adsorbed strongly on silica at pH 5 and 10 mmol/L NaCl due to the combination of electrostatic and hydrophobic attraction. Zeta potentials showed a reversal of the charge sign, which points towards bilayer type adsorption. The adsorbed amount of DPC was about 5 times larger than that of SDS at the same equilibrium concentration, pH and electrolyte concentration.
Antioxidant capacity assessment of plant extracts for green synthesis of iron nanoparticles. Fenton-like decomposition of Bromothymol Blue

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Iron nanoparticles are very efficient at removing organic contaminants, organic matter and arsenic from polluted waters due to their large surface areas, high surface reactivity and high sorption capacity [1]. Besides of that, Fenton like heterogeneous systems based in the use of iron oxides have proved to be an efficient process for the degradation of recalcitrant organic pollutants in water. Fenton reagent (a solution of Fe(II)/Fe(III) and hydrogen peroxide), underlines the generation of highly reactive hydroxyl radicals which are able to oxidize many organic contaminants such as dyes [2]. Bromothymol blue (BTB) is an example of organic dye widely investigated as a model of organic contaminant. BTB can only be chemically degraded via free-radical pathways unlike other organic dyes. Hence BTB is a good model to test the application of green synthesized iron nanoparticles in a Fenton-like decomposition reaction.

A great number of studies about NPs synthesis have been done in recent years. One of the most common methods of synthesis for metallic NPs is the reduction of metal salts in solution. Synthesis of monodisperse NPs requires controlling certain parameters affecting the NPs rate of growth, like concentration of metal salts, viscosity of solvent, strength of reducing agents, etc. In addition, in most of the cases a stabilizing agent is needed to avoid the aggregation of synthesized nanoparticles. Traditional synthesis routes are expensive and most of the reactants used in these chemical routes are toxic to the environment and the living systems. As an alternative to traditional techniques of NPs production, the green synthesis methods arise, based on the use of biocompatible reagents to reduce the toxicity of the manufactured nanoparticles and the environmental impact of the by-products. Nowadays most of studies of green synthesis of NPs are developed using plant extracts [3]. Plant extracts play a double role in NPs synthesis process, they do not only mediate the reduction of metal salts but also act as capping agents to stabilize the produced NPs. The diversity of natural antioxidants makes difficult to quantify them individually in a complex matrix such as a plant extract. Therefore, a great number of assays to determine the total antioxidant capacity (TAC) of natural matrices are employed. A combination or at least two different methods is strongly recommended to determine the antioxidant capacity of natural compounds.

In this work water extracts from different natural sources have been studied to evaluate their antioxidant capacity and their potential to form metal nanoparticles from aqueous solutions. Two traditional test, Folin-Ciocalteu assay and DPPH radical scavenging capacity experiments were compared with the most recent method based in the formation of silver nanoparticles. The silver nanoparticle antioxidant capacity method was optimized for its application in the characterization of the extracts selected in this work, kinetic studies and extract concentration effect were also evaluated and nanoparticles obtained were characterized by transmission electron microscopy and dynamic light scattering. Among the extracts studied, oak, eucalyptus, white thyme and green tea showed the highest values of antioxidant capacity in the three characterization methods. The synthesis of iron nanoparticles using eucalyptus extract demonstrated the efficiency of plant extract to form metallic nanoparticles from aqueous metal salt solutions. This green synthesis was optimized under several experimental conditions, which allows obtaining different iron oxide nanoparticles in terms of formulation, size and magnetic properties. Once synthesized, iron oxide nanoparticles were applied in the Fenton-like degradation of Bromothymol Blue.

References

The authors thank Ministerio de Economía y Competitividad for the financial support through the research Project CTM2012-37272, cofounded with the FEDER programme.
Effect of flow interruption and subsequent ionic strength reduction on silver nanoparticle transport in an undisturbed loamy sand soil

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Silver nanoparticles (AgNP) find a wide application field due to their antibacterial property. Through the high consumption of AgNP a discharge into the environment is likely. In the environment, different rain events and dry periods alternate and this can influence the transport behavior of nanoparticles like AgNP in soil. Unsaturated column experiments with an undisturbed loamy sand soil were conducted to investigate the influence of flow interruption (simulates rain and no-rain weather conditions) and ionic strength reduction after flow interruption (simulating the low ionic strength of rain) on the transport and retention of surfactants stabilized silver nanoparticles (AgNP) and were compared to continuous irrigation. To determine breakthrough curves (BTCs) Ag concentrations were analyzed by ICP-MS in the effluent. The transport results were analyzed with a numerical model using the code HP1 (Hydrus-PhreeqC). The BTCs of AgNP showed a break-in due to flow interruption compared to continuous flow conditions. Interrupted flow resulted in less mobility and more AgNP retention in soil. Ionic strength reduction after flow interruption enhanced AgNP mobility in soil. The numerical model of CFT-DLVO theory with transient flow and hydro-geochemistry fitted well with the measured AgNP BTCs and indicated an involvement of air-water-interface on AgNP retention in unsaturated soil.
Functionalized Surfaces with Tailored Wettability Determine Influenza A Infectivity

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Surfaces contaminated with pathogenic microorganisms contribute to their transmission and spreading. The development of “active surfaces” that can reduce or eliminate this contamination necessitates a detailed understanding of the molecular mechanisms of interactions between the surfaces and the microorganisms. Few studies have shown that, among the different surface characteristics, the wetting properties play an important role in reducing virus infectivity. Here, we systematically tailored the wetting characteristics of flat and nanostructured glass surfaces by functionalizing them with alkyl- and fluoro-silanes. We studied the effects of these functionalized surfaces on the infectivity of Influenza A viruses using a number of experimental and computational methods including real-time fluorescence microscopy and molecular dynamics simulations. Overall, we show that surfaces that are simultaneously hydrophobic and oleophilic are more efficient in deactivating enveloped viruses. Our results suggest that the deactivation mechanism likely involves disruption of the viral membrane upon its contact with the alkyl chains. Moreover, enhancing these specific wetting characteristics by surface nanostructuring led to an increased deactivation of viruses. These combined features make these substrates highly promising for applications in hospitals and similar infrastructures where antiviral surfaces can be crucial.
Synthesis and structural study of uniform and monodispersed platinum doped anatase TiO₂ nanoparticles

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In this work a new synthesis method of uniform and monodispersed platinum doped TiO₂ anatase nanoparticles is presented. The resulting material is a good candidate for the energy storage in batteries and solar fuel cells. Synthesis were made using a modified gel-sol technique by seeding of TiO₂ anatase in order to obtain uniform and monodispersed doped nanoparticles. Four kinds of seeds were made at 0% (pure anatase), 1%, 5% and 10% [Pt]/[Ti] molar mass ratio, four kind of nanoparticles from seeds previously synthesized and a pure anatase system without seeds. Energy dispersive X-ray analysis showed platinum respectively at 1.3, 10.7 and 10.1 weight percent. XRD theoretical studies by Rietveld Refinement using FULLPROF suit showed a good agreement assuming two phases, I4₁/amd in tetragonal system related from anatase dioxide and Fm-3m in cubic system from Pt. The intensity of the second phase increases with dopant until obtaining the amorphous structure at the highest doped value. Microstrain information from software showed average crystallite sizes are close to sizes obtained from TEM pictures. For first and second phases respectively 9.200±0.003 nm and 8.825±0.002 nm for doped sample at 1%, 3.888±0.002 nm and 9.541±0.000 nm for doped sample at 5% and 3.867±0.0014% and 3.8671±0.0000% average maximum strain for both samples. Histograms from TEM pictures showed nanoparticles average size of 19.23±0.77 nm and 19.67±0.70 nm for 1% and 5% respectively. The interplanar distance of anatase obtained through software (0.35 nm) was verified by direct measurements in TEM pictures.
Development of magnetic hybrid materials obtained by green synthesis for arsenic removal

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Nanoparticles (NPs) are materials with a size between 1 and 100 nm, that show high reactivity, surface areas and a tuneable nature of several properties. The great number of applications of nanoparticles in very different fields like cosmetics, biomedicine, food or environmental remediation, makes necessary to find efficient and low cost methods of synthesis. The use of green synthetic routes has increased in the last years as they are inexpensive processes where the use of toxic reagents is avoided. One of the most extended green technique to synthesize NPs is the use of plant extracts as reductants of metallic salts. Plant extracts contain in their structure metabolites like phenols, terpenoids or carbohydrates, that provide the extracts reducing capacity. This method is a simple, low cost and eco-friendly process, where the plant extracts play a double role reducing the metallic salt and stabilizing the synthesized NPs [1].

Although the small size of NPs is responsible of their special properties, it makes difficult their application in some fields like water treatment owing to the complicate separation of the material from solution. The immobilization of NPs onto porous solids makes easier their separation from the effluent; it also enhances their mechanical strength and stability and allows their reuse. Chitosan, a natural polymer, is one of the most extended immobilization matrices. This polymer presents excellent biological properties, is a good biosorbent and can be moulded in different shapes [2]. The immobilization of synthesized NPs onto chitosan beads leads to the formation of organic/inorganic hybrid materials suitable to be used for water treatment.

Arsenic pollution constitutes a serious problem in many areas of the world like China, India or Bangladesh. Its apperance in natural waters results in several diseases like nausea, pigmentation changes and cancer. In 2001 the US-EPA established 10 µg·L⁻¹ as the recommended arsenic limit value in waters. Several studies show the affinity of arsenic for (hydro)oxides of Al, Mg or Fe. Arsenic binds the oxides by formation of outer/inner-sphere complexes. Therefore, the use of this kind of compounds as sorbents arises as a good way to remove arsenic from water [3, 4].

In this work a green synthesis process to obtain iron oxide NPs was developed using eucalyptus extract and an iron salt. The process was optimized varying the amounts of reductant and metallic salt. Obtained iron oxide NPs were characterized by TEM micrographs. The immobilization of synthesized iron oxide NPs onto chitosan beads under precise conditions, leads to the formation of magnetic hybrid materials. The XRD pattern of these materials shows peaks that match with a structure similar to maghemite for those materials showing magnetic properties. The use of the new hybrids as sorbents in an arsenic sorption process showed excellent results. pH dependence, kinetic and equilibrium studies were done. Furthermore, the capacity of this material to be used for large scale processes was also evaluated by a continuous flow study. A column filled with beads of the magnetic material was used to treat a large volumen of polluted water with succesfull results.

References

Acknowledgements: The authors thank Ministerio de Economía y Competitividad for the financial support through the research Project CTM2012-37272, cofounded with the FEDER programme.
Interaction biofilm-arsenic in freshwater environments

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Arsenic (As) is a highly toxic metalloid widespread in the environment, which causes severe and numerous health problems worldwide. The mobility and toxicity of As depends strongly on its chemical form. AsIII is more mobile and toxic than AsV, and inorganic As is generally recognized as more toxic than organic forms. Epipsamic biofilm (EB), commonly found in water-sediment interfaces, has been identified as responsible for the increase in As retention in freshwaters environments, for the inhibition of the appearance of AsIII and for the detoxification of As by a serie of methylation cascade reactions. The aims of this study are: (1) to evaluate the effect of chronic AsV exposure on the growth of the autotrophic components of EB from sediments with low and high As concentrations, (2) to determine the evolution of total As concentration and its speciation in the overlying water, and (3) to explore if biofilms grown on sediments contaminated with As may develop tolerance to this element. With this purpose, sediment samples were taken from the Anllóns River in two sites located upstream (low As content, named as LA) and within the mineralized As-Au area (high As content, named as HA). The growth of EB onto sediments, under increasing As concentrations (0, 0.3, 1, 3, 10 and 30 mg L⁻¹), was monitored over the experiment using a PHYTO-PAM device. The experiment was carried out in an incubation chamber with controlled conditions of light (12:12 h light:dark cycle), temperature (20 °C), and air-supply. Aliquots of 2 mL of the overlying water (< 0.45 µm) were taken for each system to determine the evolution of total As concentration and its speciation by ICP-MS and HPLC-ICP-MS, respectively. The results showed an increasing delay of the biofilm growth with the As dose. The biofilm growth does not begin until day 9 for the highest As concentration. Once the lag phase is overcame, the biofilm grows to a similar biomass in all samples. In general, the photosynthetic efficiencies of the biofilm-autotrophic population decreased with increasing As concentrations, evidencing the effect of As on the physiological status on these microorganisms. The analysis of algae distribution showed that green algae decreased with time and that cyanobacteria and diatoms dominated in the biofilm at the end of the experiment. No clear effect of As concentration is observed. As concentrations in the overlying water drastically decreased over the experiment. In HA systems, As removal reached 60-90% at day 4 and then progressively decreased up to around 97 %. As removal was more pronounced in LA systems, where it reached 97-99% at day 4. This effect was attributed to their finer texture and higher organic matter content, providing more sorption sites for As retention. Based of the observed results, no tolerance was evident for biofilms from previous polluted sites, although As toxicity was low for all the systems studied.
Sorption of Cu, Ni and Zn by pine bark compost using a lab permeable reactive barrier device

Hernández-Huerta, D.¹, Cancelo-González, J.¹, Martíñá-Prieto D.¹, Barral M.T.¹


Permeable reactive barriers (PRBs) are efficient and cost-effective systems for groundwater remediation. They consist of a screen perpendicular to the flow of contaminated groundwater filled with a material capable of adsorbing, precipitating or degrading pollutants. Waste materials used as reactive substrates for the construction of PRBs are of particular interest due to the possibility of their reuse and their generally lower cost. With this aim, the Cu, Ni and Zn sorption capacity of pine bark compost (PB) was evaluated using an experimental device, which reproduces a permeable reactive barrier at the laboratory scale. Percolation experiments were carried out with a mixture solution prepared with 50 mg L⁻¹ of Cu, Ni and Zn in 0.01M KNO₃, followed by a leaching step with the saline background. The results show that PB is a highly efficient filler for PRB with retention ranging from 92 to 99% (Cu>Ni>Zn). The metals retained by the filling material are strongly fixed, since low desorption was detected by leaching with the saline background (0.3, 1.8 and 4.1% for Cu, Ni and Zn, respectively). This behaviour minimizes the risk of release of the heavy metals retained by the material of the barrier in the event of it being traversed by water not contaminated. The mechanism for the retention is mostly complexation with organic matter as it is demonstrated by the high extraction efficiency of the strong complexant EDTA. Cu exhibited the highest sorption and the lowest desorption due to its higher affinity to organic matter, corroborated by the geochemical modelling of the extracts by Visual MINTEQ. The results of this study point out that pine bark compost is a potential candidate for the retention of cationic metals in a permeable reactive barrier.
Compensation of reactive power by FACTS in a power system

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In this paper we have studied the behavior of unpolluted without static compensator and their presence grid. This work is to improve the optimum performance of the compensation of the the reactive power Q and those of the profile or voltage plane taking into account the constrains of security of the electricity grid. To do this we have chosen the FACTS devices in particular SVC using the Newton Raphson method for solving the problem of load flow. The validation of this choice is made by a simulation MATLAB software on a standard network to 6 busbar and to better understand the behavior of the power network a comparison was made on the tests in the presence of SVC network and absence of SVC taking into account the total active losses.

The equivalent circuit of the electrical network is deduced:

![Figure 1: Schematic diagram of the circuit per phase](image1)

The numerical results are show in table 1 and figure 2.

<table>
<thead>
<tr>
<th>JDB</th>
<th>V [PU]</th>
<th>θ [degree]</th>
<th>Pd [PU]</th>
<th>Qd [PU]</th>
<th>Pg [PU]</th>
<th>Qg [PU]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9795</td>
<td>-12.7050</td>
<td>0.55</td>
<td>0.13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.9622</td>
<td>-12.1677</td>
<td>0.30</td>
<td>0.18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>-11.9971</td>
<td>0.50</td>
<td>0.05</td>
<td>0</td>
<td>-0.5</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>-9.7665</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.5</td>
</tr>
<tr>
<td>5</td>
<td>1.100</td>
<td>-2.9560</td>
<td>0</td>
<td>0</td>
<td>0.5010</td>
<td>0.1344</td>
</tr>
<tr>
<td>6</td>
<td>1.000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.9362</td>
<td>0.1201</td>
</tr>
</tbody>
</table>

Total active losses in the network: 8.7177 [MW]

Power factor cos ϕ = 0.895

![Figure 2: Schematic diagram of the circuit per phase](image2)

In this work, we tried to illustrate the usefulness and efficiency of voltage control by inserting the SVC. MATLAB software has given very satisfactory results for different cases of simulation, where we successfully improved tension JDB and an appropriate distribution of reactive power.

References
Fault detection by use of parameter estimation in systems

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A parameter estimation technique based on the least squares method with or without forgetting factor is presented in this work. This technique is applied to power supply systems, with or without defects. An evaluation in computer simulation of a coil with an iron core with or without fault short circuit turns, lets discuss the quality of the estimation of the physical parameters of the coil. The method of recursive least squares are used to identify the parameters of the numerical models of physical processes or signals. The idea is to minimize a quadratic criterion corresponding to the square of the error at time k, between the model output and output value of the process or of the signal, which will be modeled. The principle of the identification process is shown in the diagram of principle (figure 1) [3]

![Figure 1: General principle of identification](image)

The distribution of estimates physical parameters follows quasi-normal distributions whose parameters are detailed in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{est}$</td>
<td>3.5028</td>
<td>$&lt; 10^{-4}$</td>
</tr>
<tr>
<td>$r_{purs}$</td>
<td>88.6444</td>
<td>8.24</td>
</tr>
<tr>
<td>$l_{est}$ ($x 10^{-3}$)</td>
<td>40.42</td>
<td>$&lt; 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 1: Distribution of estimation for series of 1000 acquisition sequences

In this paper, the parameter identification methods based on recursive least squares to estimate the physical parameters of the iron-core coil are applied. The results show that the estimated values are correct, but the convergence is slow and sensitive to measurement noise. The application of the MCR method with forgetting factor allows increasing the speed of convergence.

In future work, identification methods will be used for the detection and diagnosis of faults. Indeed, we have demonstrated the sensitivity of the identified parameters to a fault. Furthermore, the proposed methods allow us to construct a set of reference models with and without fault will be used for the detection (compared to the model without fault) and diagnosis (comparison with models dysfunction).

References

Porous Activated Carbons Produced from Molasses as CO₂ Sorbents

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As a carbon source we chose sugar beet molasses cheap, economical and sustainable industrial waste product. Use of this waste as activated carbon (AC) precursor was described two times [1, 2], and the method of production was different from utilized by us. According to the our knowledge the adsorption of CO₂ on ACs obtained from molasses was not described up to now.

Dense liquid – molasses, has been mixed with grounded potassium hydroxide. The dry masses to KOH ratio was equal to 1. The mixture was left for 3 hours and then dried at 200 °C for 19 hours. Materials were grounded and pyrolysed at temperature 600 – 900 °C. After pyrolysis materials were grounded and washed with water to neutral pH, soaked with HCl (0.1 mol/dm³) for 19 hours and washed with water again. Specified surface area (SBET) of obtained ACs, total pore volume (Vtot), micropore volume (Vmic) was obtained on the basis of nitrogen sorption at 77 K. The CO₂ adsorption at temperature 0 °C was measured by volumetric method. XRD and SEM method were used for characterise ACs.

Image 1 shows image of activated carbon produced at 750 °C. Deep cavities can be seen. The others images of ACs looked similar. The XRD spectra were typical of ACs. The results of nitrogen sorption are presented in Table I. High specific surface areas (above 1100 m²/g) were obtained. The highest specific surface area of 2828 m²/g was received. The total pore volume above 1 cm³/g was produced at the temperature higher than 750 °C. The micropores contribution in all the ACs was very high, even 80%. Table 1 lists CO₂ uptakes measured at 0 °C. The CO₂ uptakes ranged from 3.13 to 4.89 mmol/g.

<table>
<thead>
<tr>
<th>Temp [°C]</th>
<th>S_{BET} [m²/g]</th>
<th>V_{tot} [cm³/g]</th>
<th>V_{mic} [cm³/g]</th>
<th>CO₂ ads. [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1106</td>
<td>0.493</td>
<td>0.398</td>
<td>4.35</td>
</tr>
<tr>
<td>650</td>
<td>1256</td>
<td>0.326</td>
<td>0.263</td>
<td>3.13</td>
</tr>
<tr>
<td>700</td>
<td>1727</td>
<td>0.839</td>
<td>0.609</td>
<td>3.56</td>
</tr>
<tr>
<td>750</td>
<td>2305</td>
<td>1.725</td>
<td>0.533</td>
<td>4.89</td>
</tr>
<tr>
<td>800</td>
<td>2427</td>
<td>1.253</td>
<td>0.823</td>
<td>4.46</td>
</tr>
<tr>
<td>850</td>
<td>2828</td>
<td>1.839</td>
<td>0.791</td>
<td>3.96</td>
</tr>
<tr>
<td>900</td>
<td>1761</td>
<td>1.053</td>
<td>0.571</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Table 1: Textural properties and CO₂ adsorption

The ACs produced from molasses were highly porous materials and good carbon dioxide adsorbents.

References

Acknowledgement: The research leading to these results has received funding from the Polish-Norwegian Research Programme operated by the National Centre for Research and Development under the Norwegian Financial Mechanism 2009-2014 in the frame of Project Contract No Pol-Nor/237761/98/2014
Oxidation of limonene using activated carbon modified in dielectric barrier discharge plasma

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Limonene can be obtained from orange peels, which are waste from the fruit juice industry. It is widespread available, low price, renewable material. As products of limonene oxidation various compounds can be obtained: 1,2-epoxylimonene, 1,2 epoxylimonene diol, perillyl alcohol, carvone, carveol, which are very valuable intermediates for the production of food flavourings, perfumes, cosmetics, drugs, pesticides and polymers.

The research presented in this paper concerned the limonene oxidation using commercial activated carbons (ACs) EuroPh and FPV as catalyst kindly supplied by Gryfskand Sp o.o (Poland) and the same ACs, but modified in dielectric barrier discharge plasma in air.

The ACs were characterized by liquid nitrogen adsorption at 77K, XRD, IR spectroscopy, SEM and XPS. Oxidation of limonene was carried out at 80 °C and for a time up to 96 h. The molar ratio of limonene to the hydrogen peroxide or tert-butyl hydroperoxide (WNTB) was 1: 2, and the methanol concentration amounted to 95 wt%.

All the above mentioned methods, except the XPS, showed no differences between the commercial ACs, and ACs after modification in the plasma. It was found that ACs modified in dielectric barrier discharge plasma in air at atmospheric pressure caused surface oxidation and increase the C-O, keto-enol, C = O and COOH groups concentration. The table shows the contents of carbon functional groups before and after modification in plasma.

<table>
<thead>
<tr>
<th>Groups</th>
<th>EuroPh before</th>
<th>EuroPh after</th>
<th>FPV before</th>
<th>FPV after</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C. C-C</td>
<td>54.8</td>
<td>43.6</td>
<td>59.0</td>
<td>40.6</td>
</tr>
<tr>
<td>C-O</td>
<td>14.7</td>
<td>39.9</td>
<td>19.0</td>
<td>45.0</td>
</tr>
<tr>
<td>Keto-enolic</td>
<td>11.8</td>
<td>0.0</td>
<td>3.3</td>
<td>0.0</td>
</tr>
<tr>
<td>C=O</td>
<td>9.3</td>
<td>2.7</td>
<td>8.2</td>
<td>0.0</td>
</tr>
<tr>
<td>COOH</td>
<td>6.3</td>
<td>13.8</td>
<td>6.6</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Table 1: The contents of carbon functional groups before and after modification in dielectric barrier discharge plasma in air in at%. On the basis of C1s signal.

The ACs EuroPh and FPV were active in the limonene oxidation by H2O2 and WNTB. After modification EuroPh the increase in the limonene conversion and selectivity to carveol and perillyl alcohol was observed, when H2O2 was used as the oxidant. The oxidation of limonene by WNTB after EuroPh modification wasn’t increased values of these functions but changed the direction of oxidation. The allylic oxidation at position 7 in the limonene molecule (the formation of perillyl alcohol) was observed. Before modification over EuroPh epoxidation of the unsecured bond at the position of 1-2 in the limonene molecule (formation of 1,2-epoxylimonene) took place.

The conversion of limonene and selectivity to 1,2-epoxylimonene diol over FPV after treatment with the plasma was increased when H2O2 was used. The oxidation of limonene by WNTB over modified FPV didn’t take place.
Enhanced photocatalytic activity and antifungal efficiency of metal-doped TiO$_2$ nanocomposite coatings applied on wall paints

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The deterioration of walls and wall paints caused by the growth of microorganisms is not only an aesthetical problem but it also has a very negative effect on physico-mechanical properties of walls. Since the toxic biocides with a wide-protection range are forbidden by law (EU regulations, Biocidal Products Directive 98/8/EC) [1], there is a need for an efficient biocide replacement in order to keep the environment safe as well as to be effective against the fungal pollution.

It is well known that metals with higher oxidation states increase the photocatalytic activity [2]. This is found to be dependent on the concentration of the doping cations [3]. Therefore, in this study the use of molybdenum doping in TiO$_2$ nanocomposite suspension was proposed. The obtained material could be used for application on wall paints in order to enhance the photocatalytic activity and consequently, the antifungal efficiency.

The photocatalytic active nanocomposite based on TiO$_2$ and molybdenum-layered double hydroxides (Mo-LDHs) was synthesized by a wet impregnation technique [4] with 10 and 3% w/w TiO$_2$. The freshly prepared suspension was applied by spray technique on the surfaces of the commercial white wall paints serving as a proper porous sample system in order to obtain reliable results for practical use. The photocatalytic behaviour of the coated samples was investigated by monitoring model organic dye concentration changes under the UV-Vis irradiation [5] (UV-Vis absorption spectroscopy) and degradation of the model organic components in a gas medium (FT-IR spectroscopy at gas/solid interface). Antifungal efficiency assessment was performed by monitoring the fungal growth (artificial ageing conditions) and by quantification of its development in both the fungi media (agar) and on the coated wall paint surfaces kept together in petri dishes by the method proposed in the reference [6].

The durability of the developed photocatalytic coating was tested by simulating real environmental conditions (rinsing durability) [7]. The characteristics of the obtained coating: photocatalytic activity, colour change and antifungal efficiency were performed before and after the rinsing test.

The results of photocatalytic activity and antifungal efficiency of the developed Mo-LDHs were compared to a pure TiO$_2$ coating and to the results of previous study (TiO$_2$ nanocomposite coatings doped with the metals with lower oxidation states) [6]. The obtained results indicate a possibility of both the remediation of contaminants and the prevention of pollution.

References

Assessment of air pollution in port of Algiers, using energy dispersive X-ray fluorescence

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Abstract:
The industrial sector in Algeria is very poorly studied from the perspective of evaluation of air pollution and its impact on the environment. The sector suffers from a lack of data. Pollution sources are many and their impact is unknown. We propose in this work to study the air pollution levels in the port of Algiers by suspended particles and heavy metals. The samples for aerosols, collected from port, were analysed using the Wavelength-dispersive X-ray fluorescence (WXRF) method in order to determine the concentrations of different elements. Our qualitative analysis of spectral peaks showed that the samples contained K, Ca, Pb, Fe, Mn, Ni, Na.....
Isolation and Characterization of Ureolytic Bacteria to Precipitate Calcium Carbonate for Heavy Metal Immobilization in Mine Soil

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Acid mine drainage occurrence is a serious environmental problem in mining industry. It usually contains high levels of metal ions, such as iron, copper, zinc, aluminium, and manganese, as well as metalloids of which arsenic is generally of greatest concern. It causes mine impacted soil pollution with mining and smelting activities, fossil fuel combustion, and waste disposal. In this study, 3 bacterial strains able to produce urease constitutively, even in the heavy metal highly contaminated soils from a mine impacted area, and were isolated. Each isolate was characterized with respect to morphology, growth conditions, 16S rRNA gene sequence identity and the urease specific activity each isolate was measured. All isolated bacterial strains were identified Sporosarcina pasteurii with more than 98% of similarity, therefore they were named Sporosarcina sp. KM-01, KM-07, and KM-12. The heavy metals were detected from the collected mine soils containing bacterial isolates as Mn(170.50 mg/kg), As(114.05 mg/kg), Zn(92.07 mg/kg), Cu(62.44 mg/kg), and Pb(40.29 mg/kg), respectively. Strain KM-01, KM-07, and KM-12 strains were shown to be able to precipitate calcium carbonate using urea as energy source amended with calcium chloride. SEM-EDS analyses showed that calcium carbonate was successfully produced and increased with time. To confirm the calcium carbonate precipitation ability, urease activity and precipitate weight were measured and compared in the present study. This makes the general application of biomineralization process based on stimulation of urea hydrolysis possible and potentially useful for a variety of soil bioengineering and environmental bioremediation applications. Considering the strains isolated area, these results also demonstrate that all isolated bacterial strains could potentially be used in the bioremediation of acidic heavy metal contaminated mine impacted soil.
Copper, manganese, zinc and chromium accumulation in three common Poaceae species on the Romanian Black Sea littoral

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Cu, Zn, Mn and Cr phytoaccumulation potential was screened for in three common Poaceae species, *Hordeum murinum* L. (wall barley or false barley), *Leymus racemosus* ssp. *sabulosus* (M. Bieb.) Tzvelev (mammoth wild-rye) and *Lolium perenne* L. (perennial rye-grass or winter rye-grass), abundantly growing, along the Black Sea Coast, Constanta area, Southeastern Romania.

The concentration of the selected heavy metals was analyzed though Atomic Absorption Spectrometry method in samples of aboveground plant organs and soils, using ContrAA 700 AAS, Analytik Jena AG, Germany, at the metals specific wavelengths, 324 nm (Cu), 279 nm (Mn), 213 nm (Zn), 357 nm (Cr). To assess the potential for phytoaccumulation, the Biological Accumulation Coefficients (BAC) were calculated.

Considering the minimal thresholds widely accepted in literature for Cu, Mn Zn and Cr hyperaccumulators, none of the selected species can fit in this category. The highest average of copper concentration (5.45 ppm) and chromium concentration (9.905 ppm) was found in *Hordeum murinum* L. For manganese, the highest value was found in *Lolium perenne* (104.08 ppm), while for zinc, the maximum was reached in *Leymus racemosus* ssp. *sabulosus* tissue (62.95 ppm).

BAC values showed that all species are manganese “excluders”, with a remarkable maximum value of 0.55 in *Lolium perenne*. All species had average BAC above 1 for Cu and Zn, with a maximum in *Leymus racemosus* ssp. *sabulosus* (4.85 and 2.98, respectively). However, there was a significant variation among individuals, usually, a high metal content in plant tissue being associated with low metal concentration in soil. The exception was *Lolium perenne* L., with BAC constantly above 1 (average BAC of 2.27 for Cu and 1.69 for Zn).

These results show an increased potential for phytostabilization of copper- and zinc-rich soils and open the way for phytoextraction studies.

References


Strontium adsorption on kaolinite at low Sr\(^{2+}\) concentration

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Strontium (Sr-90) emitting beta particles is harmful to human health. After the nuclear power plant accident in FUKUSHIMA, radioactive Sr-90 is detected near the disaster site. Therefore, the adsorption behavior of Sr\(^{2+}\) to soil particles, especially at low Sr\(^{2+}\) concentrations, deserves attention. In the present research Sr\(^{2+}\) adsorption on kaolinite at low Sr\(^{2+}\) concentration has been investigated at pH 4 and 6.5 at different NaCl solution concentrations (10\(^{-4}\) to 10\(^{-2}\) M). Iriki kaolinite (98.1% of kaolinite, 1.9% of alumite) particles <2 \(\mu\)m diameter were used and the adsorption experiments were conducted by the batch method.

The Sr\(^{2+}\) adsorption isotherms at different conditions are depicted in fig.1. The double logarithmic plots are about linear (slope \(\approx 1\)) at low Sr\(^{2+}\) concentrations, but level off at higher concentrations. This implies that, at given conditions, the distribution coefficient, \(K_d = \frac{\{SrX_2\}}{[Sr^{2+}]_{eq}}\), where \(\{SrX_2\}\) and \([Sr^{2+}]_{eq}\) are the Sr\(^{2+}\) adsorption (mmol/g) and Sr\(^{2+}\) eq. concentration (mmol/L), decreases with increasing Sr\(^{2+}\) conc., which is mainly because the adsorption sites on kaolinite become progressively occupied by Sr\(^{2+}\). The Sr\(^{2+}\) adsorption decreases with decreasing pH and increasing [NaCl]. The initial \(K_d\) at pH 6.5 is about 13 times larger than that at pH 4.1 at 0.001M NaCl, because the proton dissociation of edge sites of kaolinite increases with increasing pH. At pH 6.5 and increasing NaCl concentration (10\(^{-4}\) to 10\(^{-2}\) M) the initial \(K_d\) values decrease by about a factor 50 because of adsorption competition with Na\(^+\) on planes and screening of the electrostatic attraction at the edge surface. Clearly, pH and Na\(^+\) concentration influence the adsorption of Sr\(^{2+}\) on kaolinite strongly.

The surface charges of kaolinite are located on basal planes and edges. They consist of different site types: on the edges aluminol and silanol surface groups and on the basal planes negative sites due to isomorphic substitution. The formation of inner- and outer-sphere complexation of Sr\(^{2+}\) and Na\(^+\) on these sites was examined by applying the charge distribution and multisite complexation model (CD-MUSIC). The CD-MUSIC model predicted that outer-sphere complexation of Sr\(^{2+}\) and Na\(^+\) on the kaolinite surface is predominant at pH 6.5 and Na\(^+\) ranging from 10\(^{-2}\) to 10\(^{-4}\) M, see fig 2.
Study on the photocatalytic degradation of nitrotoluene from water using heavy metal doped titania

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Using a semiconductor as the photocatalyst for the removal of organic compounds has become a promising water treatment technology with the best prospect of exploitation and utilization. TiO2 is a suitable photocatalyst but its activity is mainly confined to the UV region of solar radiation [1-2]. In order to explore efficient visible light induced photocatalysts, much scientific effort has been conducted in recent years to reduce its band gap to make it suitable for harvesting visible light from solar radiation. One feasible approach consists of doping oxide semiconductor with transitional metal.

The photodegradation of nitrotoluene (NT) was carried out in a laboratory scale UV reactor - Heraeus system using a medium-pressure mercury (λ = 300-500 nm). The lamp equipped with a quartz water cooling jacket is immersed in the center of the reactor containing the pollutant solution. The photon's flow of the emitted radiations was determined by ferrioxalate actinometry [3] and a value I0 = 6x10^-6 einstein s^-1 was found. Doping of TiO2 with heavy metals like Fe(0.5 wt.%), Co(1wt.%), Ni(1wt.%) can efficiently catalyze the degradation of NT under UV- VIS light irradiation. The Fe-TiO2 catalyst was found to be more efficient than Co or Ni doped TiO2.

Solutions with 3.14 x 10^-4 M pollutant content were photo-oxidized in the following working conditions: pH = 7; photocatalyst dose = 200 mg/L; irradiation time = 30 – 240 minutes. Prior to irradiation, the photocatalyst powder was added to the samples, and solutions were bubbled with air (50 L/hour), in the dark, for 30 min.

The kinetics of nitrotoluene degradation and organic nitrogen mineralization was assessed and pseudo-first order rate constants were calculated. The experimental data verify the Langmuir-Hinshalwood model showing that the degradation process occurs on the catalyst surface. Fe doped photocatalyst (0.5 wt.%) showed a considerable better behaviour in respect to pollutant degradation than Co and Ni (1wt.%) doped titania catalysts.

Finally the energy per order of magnitude, E EO expressed in kWh/m3/order was calculated in order to assess the process efficiency with respect to the electrical energy consumption associated with nitrotoluene removal through photocatalysis process. For optimum operating conditions the values obtained was 11.03 kWh/m3/order, which are acceptable value in terms of process costs.

References

Acknowledgement: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI UEFISCDI, project number PN-II-PT-PCCA-2011-3.1-0031
Cr(VI) removal from hybrids materials based on humic acid

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Humic acid (HA) are macromolecules present in terrestrial and aquatic environments originated from biological and/or chemical decomposition of organic residues. Due to the high contents of oxygenated groups, such as hydroxyl, carboxyl and phenolic groups these substances are highly chemical reactive. However, at pH values higher than 2 the HA are soluble in aqueous solution. To improve the stability and the ability to interact with contaminants, we have synthesized a hybrid based on HA e three different alkoxysilanes: tetraethylorthosilicate (HWA), (3-aminopropyl)triethoxysilane (HOA), and N-[3-(trimethoxysilyl)propyl]ethylenediamine (HTA) by sol-gel route. The materials synthesized were characterized by diffuse reflectance Fourier infrared spectroscopy (DRIFT) and small-angle X-ray scattering (SAXS). The stability of the materials were evaluated in different pH values [1]. The three different hybrid materials were evaluated as their capacity to remove Cr(VI) species from aqueous solution. The assays to evaluate the Cr(VI) were made in batch during 7 days. The DRIFT and SAXS analysis showed the formation of three new hybrid materials, and that the alkoxysilane employed in the reaction governed the properties of these materials. All materials were stable in aqueous solution until pH 10. The three materials showed a higher capacity to remove Cr(VI) species from solution. Although the HOA sample showed a slower kinetic than HWA and HTA samples, the percentage of removal were 95 % for all hybrid materials. These materials have a great potential in the removal of Cr(VI) species and might be an alternative in the decontamination of these metallic species from aquatic environments.

References

Acknowledgement - The authors thank to FAPESP (Project 2013/27039-4).
Hybrids materials based on humic acid and clays for agricultural application

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Organic matter (OM) and clays are the two most important components of soils. Humic substances (HS) represents the main fraction of the OM. These substances are separated into humic acids, fulvic acids and humin. The humic acid (HA) represents the insoluble fractions in water under acid medium (pH < 2), and due their complex chemical composition, these substances affect the behavior of the different contaminants in aquatic and terrestrial environments. In soils, clays and HA are often associated, and both can contribute to sorption of inorganic and organic contaminants. On the basis in the natural environments, the aim this present work were to associate and improve the properties of HA and clays syntheizitng a new hybrid material based on both materials mimicking the soil fractions that are naturally composed by complexes mixtures between clays and OM. Two different clays were used in the syntheses of the materials: kaolinite intercalated with dimethylsulfoxide (DMSO) and bentonite. The hybrid materials were characterized by X-ray powder diffraction (XRPD) and Fourier transform infrared spectroscopy (FTIR). The results showed that the bentonite have a better interaction with the HA than kaolinite with DMSO. The XRPD reveals that DMSO molecules were removed from kaolinite interlayer space and at the same time HA molecules cannot access the confined space of kaolinite confirmed by the decreasing of basal spacing from 11.2 Å to 7.2 Å. Bentonite-HA hybrid showed an increase on basal spacing confirming the presence of HA between interlayer space of this clay. The FTIR showed different association of the HA for the clays. These hybrid materials prepared have a great potential applications in the adsorption of the micronutrients used in different crops, and we are evaluating their use as agricultural and environmental friendly fertilizers.

Acknowledgement - The authors thank to FAPESP (Project 2013/27039-4), CAPES and CNPq.
Investigation of metal load variations through tracer injection

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The environmental mobility and toxicity of mine waste contaminants such as Pb, Zn, Fe and Cd is primarily driven by spatial and temporal variability in geochemical (e.g. pH, Eh, O₂) and hydrologic (e.g. discharge, permeability, conductivity) processes. Quantifying these processes can be challenging, especially where mining has profoundly modified natural hydrological pathways. The purpose of this work is to quantify flow variable metal loads and identify the role of colloids in metal transport in mining-impacted river catchments. Such investigations are crucial to understand spatial and temporal patterns in environmental risk posed by metal-rich mine waste. The study area is a historic metal mining area, Wemyss Mine, located in the headwaters of Nant Cwmnewyddion catchment (central-east Wales, UK). The stream also receives water from the metal-rich Frongoch adit. Further downstream, the Nant Magwr and Afon Ystwyth fail to meet water quality guidelines due to high Zn and Cu concentrations.

Given this complex situation, first, a continuous tracer injection coupled with synoptic water sampling will be used to quantify spatial patterns of stream metal loading and to identify zones of contaminant attenuation and release. Second, water samples will be collected to determine the relative importance of dissolved and colloidal metal transport. From this investigation, we hypothesise that elements will exhibit different geochemical patterns along the course of the river. Non conservative elements should have an irregular spatial pattern and different concentration related to different filtrations. This would suggest a likely role of colloids in driving non conservative metal fate. Considering water contamination in function of only dissolved elements can limit hazard assessments that may ignore important metal storage, transport and release. In dynamic systems, such as natural ecosystems, elements can interact differently with colloids as a function of their shape, surface charge or adsorbed elements. Understanding how colloids transport metals, or which geochemical and hydrological settings guide their processes and movements, needs further field investigations and laboratory analysis.
Iron oxide and organic matter composites: their effect on contaminants removal

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Nanosize colloidal particles present in soil and aquatic systems, such as natural organic matter (NOM) and iron (hydr)oxides, can interact via different mechanisms and control the retention, bioavailability, and bioaccumulation of trace elements. Copper and arsenic are considered as environmentally relevant inorganic pollutants involved in processes related to soil and water contamination. The study of the reactions between these pollutants and organic matter-mineral surface is important to understand the bioavailability of arsenate and copper in natural systems. A better comprehension of these processes would be helpful to solve environmental and health issues.

In the present work several organic matter-iron oxide composites were prepared. Different organic acids analogous to those present in soils, such as citric acid, tartaric acid, 4-hidroxibenzoic acid or the more heterogeneous and naturally occurring humic acid, were selected. Copper and arsenic adsorption experiments were conducted with the different composites prepared.

The obtained results reveal that the presence of organic matter is an important factor capable of enhancing or attenuating the adsorption of inorganic contaminants. NOM will slightly increase the sorption of copper (Fig. 1) in comparison with the bare iron oxide whereas its presence would prevent the sorption of arsenate due to both, electrostatic and blockage effect. On the other hand, the nature of the organic acids present in the composites seems to have a very slight effect. Humic acid and citric acid led to a larger adsorption of copper compared to the other simple organic acids.

Figure 1: Evolution of copper (Cu) adsorption with the pH over different ferricydrate (Fh) composites in presence of tartaric (Ta) and citric (Ci) acid.
Characterization of proteins associated with mercury in samples of muscle and liver tissues of filhote (Brachyplatystoma filamentosum) from the Brazilian Amazon.

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The mercury contamination pollution in the rivers of the Brazilian Amazon sets up one of the main environmental problems of the region. The consumption of fish may pose a risk to the health of these coastal communities. The determination of mercury in fish species presents difficulties due to low concentrations of these species present in these samples and also because the toxicity depends on the species mercurial analyzed [1]. In this context, the development of biomarkers related to mapping and expression of proteins associated with mercury can indicate in advance the risks related to fish contamination of Amazonian rivers. The metalomics, recent research area, enabled the integration analytical and biochemical studies of highly complex, comprising sequencing and characterization of proteins associated with metals [2]. Thus, this paper presents the mercury fractionation results linked protein of muscle and liver samples of filhote (Brachyplatystoma filamentosum) collected in Jirau region River Basin Wood - Brazilian Amazon. Initially the concentration of total mercury it was determined by graphite furnace atomic absorption spectrometry (GFAAS) in the muscle and liver samples and extracts of protein pellets obtained by fractional precipitation. Then, the muscle and liver proteome of this fish species was separated by two-dimensional polyacrylamide gel electrophoresis (2D PAGE), and mercury present in the protein spots was determined by GFAAS after acid mineralization assisted by ultrasound bath. Protein spots that had mercury were characterized by mass spectrometry with electrospray ionization in sequence (ESI-MS/MS) after tryptic digestion. The total mercury determinations indicated that the mercury concentration in the liver tissue (617±11 µg kg⁻¹) is about 1.60 times greater than the concentration of mercury in muscle tissue (378±9 µg kg⁻¹) and approximately 65% of the mercury present in samples of liver and muscle tissues are bound in protein pellets with molecular mass (Mm) less than 90 kDa, while the pellets wit molecular mass larger than 90 kDa was either not detected the presence of mercury. The mercury concentrations in muscle spots present in the range from 13.60 to 16.90 mg g⁻¹ and liver spots in the range from 33.00 to 83.40 mg g⁻¹. Based on mercury concentrations it was possible to estimate that the protein spots contained approximately one atom of mercury per protein molecule. Analysis by ESI-MS/MS allowed the characterization of eleven spots protein the following proteins and or enzymes: parvalbumin-2 (Mm = 12.40 kDa, pI = 3.80); parvalbumin alpha (Mm = 12.40 kDa, pI = 3.80); ubiquitin-40S ribosomal protein S27a (Mm = 11.60 kDa, pI = 6.10); GTP cyclohydrolase regulatory protein feedback (Mm = 13.00 kDa, pI = 4.00); transmembrane protein 186 (Mm = 14.00 kDa, pI = 4.70); Glycolipid transfer protein (Mm = 12.20 kDa, pI = 3.50); Betaine-homocysteine S-methyltransferase 1 (Mm = 12.30 kDa, pI = 6.90); Macolin-2 (Mm = 12.20 kDa, pI = 8.00); N-terminal Xaa-Pro-Lys N-methyltransferase 1 (Mm = 10.50 kDa, pI = 8.90) and GTP cyclohydrolase feedback regulatory protein 1 (Mm = 13.70 kDa, pI = 4.90)

References

Acknowledgement - The authors thank the Brazilian research funding agency ANEEL/ESBR- P&D: 6631-0001/2012/ Contract Jirau 004/2013 and FAPESP (Processes: 2010/51332-5 and 2009/54856-8) for their financial support.
Mercury fractionation in breast milk samples from lactating women of amazon region-brazil using metalloproteomics strategies.

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Mercury is a potentially toxic element present in the environment of Brazilian Amazon. This metal participates in biogeochemical cycles mediated by microorganisms in which it is chemically transformed, undergoing biomagnification and bioaccumulation in the food chain. Thus, predatory fish, which accumulate high levels of mercury, can act as vehicles by which their consumers, such as reptiles, birds and humans, are exposed to this potentially toxic element. Therefore studies related to mercury toxicity are of fundamental importance for the health and life quality of the Amazonian communities [1]. Given the above, this study sought to detect and assess possible protein biomarkers of toxicity of mercury in breast milk samples from lactating women collected from coastal communities of the Madeira River and the Negro River in the Brazilian Amazon. For this, first, total mercury was determined in the hair samples of lactating women to identify which were contaminated with mercury, and then there was obtained the proteome of the breast milk samples by two-dimensional electrophoresis (2D PAGE) after protein precipitation in acetone medium. In the protein spots obtained in the proteins fractionation of the breast milk samples, mercury determinations were carried out by atomic absorption spectrometry graphite furnace (GFAAS), where it was observed that mercury is linked in protein with molecular mass in the range of 14 -26 kDa. The determination of total mercury concentration was also carried out by GFAAS in unprocessed milk, lyophilized milk and protein pellets, with the purpose of making a mercury mass balance in relation to the concentration of this element in milk and pellets. Mass balance calculations allows us to observe that, in respect of milk samples of lactating women of Madeira River, about 85 to 95% of the mercury present in the lyophilized milk is bound in the protein fraction. Regarding the lactating women of Negro River, about 50% of total mercury is bound in the protein fraction and the difference of 51% can be bound in the lipid fraction. However, further studies in this line of research should be developed to obtain robust conclusions.

References

Acknowledgement - The authors thank the Brazilian research funding agency ANEEL/ESBR- P&D: 6631-0001/2012/ Contract Jirau 004/2013 and FAPESP (Processes: 2010/51332-5 and 2009/54856-8) for their financial support.
Efficiency comparison of single and multilayered reactive zones for heavy metals removal

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Groundwater contamination by heavy metals has been an environmental issue for a long time. Accordingly, the aim of this studies was to examine the ability of zero-valent iron (ZVI), zeolite (Z) and modified construction aggregate (MCA) to remove heavy metals from aqueous solutions. Moreover, the use of alternative material in permeable reactive barriers (PRBs) technology has been investigated. In this paper, the continuous-flow column test results by single and multilayered systems were presented. The break through times for a mobile tracer that does not sorb to the material for MCA, ZVI, Z and layered ZVI, Z and MCA were as follows: $1.28 \times 10^4$ s, $1.01 \times 10^4$ s, $1.57 \times 10^4$ s and $2.38 \times 10^4$ s. The breakthrough time ($t_{br}$) for Cd was in the range of $t_{br} = 2.93 \times 10^6$ s for MCA, through $t_{br} = 5.84 \times 10^5$ s for ZVI, to $t_{br} = 1.69 \times 10^7$ s for Z. The breakthrough time for Ni was in the range from $t_{br} = 8.16 \times 10^6$ s for MCA to $t_{br} = 1.80 \times 10^7$ s for Z. Furthermore, the breakthrough time for Zn was in the range from $t_{br} = 1.53 \times 10^6$ s for MCA to $t_{br} = 5.08 \times 10^7$ s for Z. During the experiment, the concentration of Cd, Cu, Ni, Pb, and Zn in the solution from a column filled with several materials and Cu, Zn for ZVI and Pb for column filled with zeolite was close to zero. The reduction of metal ions removal was due to high pH values of the solution (above 8.00). In addition, during the testing period, an increase of Cu and Pb concentration in the filtrate from the column filled with MCA was observed, but at the end of the experiment the concentrations did not reach the maximum values. Therefore, MCA may be recomended as a “new” alternative reactive material for PRBs technology. The test results suggest that the multilayered permeable reactive barrier is the most effective technology for long time effective removal of heavy metals mixtures. The presented test results allow to conclude that the PBR’s layer system consisting of zero-valent iron, zeolite and modified construction aggregate for a mixture of heavy metals removal is more effective than single layer system and therefore is more efficient on account of long time effective cleaning without breakthrough times for contaminates.
Comparative study of the presence of heavy metals utilizing epiphytic corticolous lichens in the Talca city, Maule Region, Chile.

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Lichens are been used as indicators of the presence of a high variety of atmospheric contaminants especially in urban and suburban cities worldwide. Due to that the lichens have no root, their mineral nutrition depends mainly on atmospheric inputs and secondly place the lack of protective cuticle and stomata, thalli can accumulate mineral elements, including heavy metals, at levels exceeding their metabolic requirements. In 1999 year in the Talca city was evaluated the presence of the following heavy metals: Cd, Cu, Cr, Fe, Pb and Zn in the lichen thalli of three species of epiphytes lichens: Parmelia flaventior, Phaeophyscia orbicularis and Ramalina striatula localized in three sectors of the city exposed to different levels of contamination sources: Sector 1: south, residential, moderate traffic, Sector 2: city center, Industrial, with high traffic and Sector 3: nord, residential, low traffic. According to the results obtained then, the more heavy metal accumulating species was P. orbicularis following by P. flaventior and R. striatula (R. ecklonii). Once the samples processed under standardized conditions, quantification of metals was performed using atomic absorption spectroscopy (UNICAMP 969) using standard addition. The validity of the analytical methodology was carried out with certified reference material from the SMR. The aims of this study were to determine these same metals in the same species, located in the same select sectors in the previous study, and compare these values with those obtained 17 years ago. It is expected that these values are equal or superior to those obtained in the past, depending on the potential for bioaccumulation of the studied species and the effect of a catastrophic event like the earthquake of 2010, which heavily impacted urban and environmental structure Talca. The samples are being analyzed. These results allow us to know which of these species have the ability to accumulate or maintain certain metals in its thalli, reaffirming their potential as bioindicators long-term in contaminated environments and that sectors of the city exhibit the highest percentages of contamination by these elements.

Acknowledgements: The authors thank to PIEI QUI-BIO Utalca, CHILE project.
Low grade heat recovery using small scale ORC systems

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Nowadays, new energy efficiency measures are being developed and improved to be placed in the market, as the only way to contribute to decrease the environmental problem. In this way, the organic Rankine cycle (ORC) is a promising technology that can take profit from renewable and waste heat sources to produce electricity. However mainly large scale plants are being constructed, due to the difficulties and lack of knowledge that involves small scale systems.

Having this into account, this work addresses various experimental projects that have been developed using small scale ORC systems. An industrial waste heat source, a solar thermal plant and a biomass boiler are the applications. Moreover attending to the experimental data available from previous works [1], an analysis to assess the environmental impact of these applications is conducted.

References

Acknowledgement
The authors thank greatly the Jaume I University for its financial support under the PhD grant PREDOC/2013/28 of ’Convocatòria d’ajudes redactorals per a la formació de personal investigador del Pla de promoció de la investigació de la Universitat Jaume I de Castelló (Spain)’.
Rapid on-line method of wastewater parameters estimation by electronic nose and computer simulations in operating WWTP

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The effluents from wastewater treatment plants (WWTPs) are discharged to water bodies or rivers, therefore can be detrimental for environment. To normalise issues pertaining to wastewater discharging many directives and regulations have been released, which determine permissible levels of pollutants in effluent stream. In order to comply with these regulations and not exceed level of particular indicators of wastewater quality, the operational mode of facilities at WWTP should be properly adjusted according to wastewater parameters of influents. These is very difficult without frequently performed measurements. Currently there are known many techniques and devices for assessment of wastewater parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), total suspended solids (TSS), oxygen uptake rate (OUR), level of phosphorus and nitrogen compounds. In spite of the far reaching improvements in automatisation of treatment process, there still isn’t developed a automatic measuring system of basic wastewater parameters. Required time for determine some parameters according to proper methodology vary from 2 hours (COD) for even 5 days (BOD₅). For the other parameters obtained by means immersed sensors, there could be problems with lack of repeatability due coating of sensors with biological film. Considerable limitation could be also a cost of professional measuring equipment. Therefore, in many local WWTP the measurement are performed very seldom and treatment process is based mainly on observations of experienced personnel. Rapid on-line method of wastewater parameters estimation by electronic nose and computer simulations could be recommended as an alternative solution in many WWTPs in comparison with traditional approach.

The aim of this study was to evaluate concepts of on-line measurement by e-nose and computer simulations for real-time control biological treatment processes at WWTP. At the first stage there was performed laboratory research at sequencing batch reactor (SBR). During the few months of experiment the COD measurements was periodically conducted using a HACH DR2800 spectrophotometer (Hach-Lange GmbH, Germany). Simultaneously the continuous measurement of e-nose was executed for the wastewater headspace. Gas sampling probe was equipped with desiccant membrane dryer e-nose device applied to measurements had an embedded array of semiconductor resistive gas sensors. Array consist of 8 sensors MOS type, temperature and relative humidity sensor. Afterward the measurements data from both techniques was compared in order to calibrate e-nose to COD prediction. As the studies have shown, it could be possible to estimate COD with high accuracy (r = 0.98). Due to the fact that COD value is estimated indirectly, method should be treated as an additional, initial measuring instrument for rapid on-line estimation of wastewater parameters as well as the device enabling early detection of untypical micropollutant or excessive biological load. Device should be also re-calibrated by cyclically carried out standard measurements of wastewater quality parameters.

At the second stage of survey the suitable model of the SBR reactor was created in GPS-X (Hydromantis) software. The GPS X dynamic simulator, based on the activated sludge model (ASM). The modeling of real-time data obtained from laboratory SBR tests were used to estimate wastewater parameters and compare results of e-nose and computer simulations in order to develop the inexpensive and fast-responding measuring for the WWTPs The elaborated method enables continuous and relatively low cost monitoring of the wastewater quality even in many key points of operating WWTP. According to obtained results the optimal operation conditions of wastewater treatment process were adjusted. Moreover the negative effect of effluent on environment as well as reduce operating costs due to electric energy saving could be achieved. Water and wastewater utilities, which run and control WWTP, are interested in optimizing the process in order to save environment, their budget and decrease the pollutant emissions to water and air. In this context, computer simulation support with on-line e-nose measurements could be cheap and very useful tool to improve the efficiency without interfering in the actual process performance.
Biofouling mitigation and related mechanisms of coating with Lysine-Glutamic acid alternating peptide

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In the form of a polymer brush, the anti-fouling characteristics of zwitterionic polymer are enhanced by a nano-hydrogel structure. In this study, the anti-fouling properties of coating with the block copolymer of Polystyrene (PS) bonded to the alternating peptide (Lysine-Gultamic acid)₁₅ were systematically analyzed. Swelling analysis of the PS-b-[{(KE)alt}₁₅] layer, provided an indication of the “anti-polyelectrolyte” effect, which was verified in the presence of NaCl using a quartz crystal microbalance with dissipation (QCM-D), atomic force microscope (AFM) and submerged bubble contact angle. Clear agreement with the NaCl effect on swelling of the coating was observed with dynamic light scattering, showing a shift in the population of micelles towards individual molecules in NaCl versus distilled water. Ultralow biofouling characteristics were shown at different levels: (i) reduced bacterial attachment; (ii) reduced adsorption of extracellular polymeric substances onto modified coated polystyrene surfaces; (iii) reduce biofilm formation on different types of surfaces (stainless steel, glass, polystyrene, and commercial reverse osmosis membrane); and improved performance of reverse osmosis membranes during desalination and biofouling conditions.
A predictive model for DMT equilibrium concentrations.

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The Donnan Membrane Technique (DMT) [1] provides the free ion concentrations of an aqueous sample. This technique relies on the selective permeation of cations (or anions) through an ion exchange membrane. For the sake of simplicity, we focus here just in the analysis of cations. The sample (or donor solution) reaches equilibrium with a synthetic acceptor solution, being both in separate compartments. DMT has been extensively used in soil extracts [2] and waters [3-5]. Equilibrium between the transferable cations means that their electrochemical potential is the same in the acceptor as in the donor solutions. After simple algebra, the activity of an analyte M in the donor solution is related to the activity of this analyte in the acceptor and the activities of a reference cation (e.g. K⁺ or Ca²⁺), so that, finally, the free concentration of analyte in the donor solution can be computed from the total concentrations (measured with ICP-MS) of the analyte in the acceptor solution and that of the reference cations in both solutions. A few DMT works have tackled food matrices such as milk [6] or wine (Lao et al. submitted). One advantage of DMT is the possibility of the simultaneous determination of various free ion concentrations. One limitation of current DMT designs (lab-cells and, to a lesser extent, field-cells) is the relatively long equilibration times to be endured.

To the best of our knowledge, the situation of equilibrium in DMT (i.e. the final concentrations), as a function of the initial concentrations of the ions in both compartments, has not been modelled. Our physicochemical model takes into account the equality of the electrochemical potentials, electroneutrality and mass balances. The predicted concentrations can be compared with carefully designed experiments where a complete monitoring of the relevant parameters (pH, Temperature, ionic strength, concentrations of anions and cations, etc.) has been in operation. The possibility of using different acceptor solutions yielding consistent values of the concentration of the determinand suggests a standard way for achieving robust analyses.

The model provides guidelines on how to tune the synthetic acceptor solution to best fit the challenges of a particular sample solution. Benefits of this model could be: i) improvement of the limit of detection, by preparing acceptors that lead to a pre-concentration of the analyte in the acceptor; ii) reduction of the equilibration time, by preparing acceptor solutions that lead to lower equilibrium concentrations of the analyte in the acceptor; iii) better capability to detect the undesired transfer of positive complexes; iv) a re-assessment of the impact of ionic strength in DMT and v) to pave the way for the search of more suitable reference cations.

References
Biological treatments of cadmium contamination continental waters with *spirulina platensis* (nordst.) Geitl. Immobilized in Na-alginate beads

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**Introduction**

Bioremediation, as a non-conventional adsorption techniques, being in situ treatment, provides a safe and economic alternative to commonly used physicochemical strategies (Eccles, 1995). The special surface properties of microorganisms enable them to absorb different kinds of pollutants from solutions (Aksu, 2001). Biological elements such as algae can profoundly influence the distribution of trace metals in natural waters. Biosorption algae was studied using *Spirulina platensis* (Nordst.) Geitl. on alginate gel. Their use as a bio-sorbent for cadmium is an effective, ecofriendly and economical alternative to existing treatments (Tangaromsuk, et al., 2002). The central aim of this study is to enhance the utilization of blue-green algae strains for cadmium removal at very low concentration (µg/L) in natural waters. Various kinetic and equilibrium aspects of cadmium (II) metal ions biosorption were studied. The pseudo-first order and pseudo-second order kinetic models were used and the equilibrium results are given in terms of the units of adsorbed metal ion concentration.

**Results:** The equilibrium uptake of cadmium (II) ion and adsorption yield (Ad%) for all cycles is shown in Table 1. The maximum adsorption yield was found to be 39.7 % for *Spirulina platensis* and 13.9 % for alginate of the initial cadmium ion concentration. For the alginate matrix, adsorption is limited by available sites; further increase in initial concentration (C₀) does not show much effect on the adsorption yield.

**Table 1: Comparison of the equilibrium adsorbed quantities and adsorption yields for each species at different initial cadmium ion concentration**

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>I Cycle</th>
<th>II Cycle</th>
<th>III Cycle</th>
<th>IV Cycle</th>
<th>VII Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Ad(%)</td>
<td>qₑ(mg/g)</td>
<td>Ad(%)</td>
<td>qₑ(mg/g)</td>
</tr>
<tr>
<td><em>Spirulina platensis</em></td>
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<td>36,5</td>
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Regarding the influence of the initial concentration of cadmium ions, in the Fig. 1 we can observe that the equilibrium sorption capacity of the biomass increased with increasing of the initial cadmium ions concentration. An increase in the cadmium concentration from 25 µg/L up to 75 µg/L leads to proportional fractions of cadmium sorption capacity from 20 up to 70 µg for a dry gram equivalent of immobilized algae for all the cycles.

**Fig.1. Evolution of equilibrium concentration of metal ions in the solution (Cₑq) as function of initial concentration (C₀) of metal ions, at a given process conditions, mg/L**

Being natural, abundant, and cheap algae biomass such as *Spirulina platensis* (Nordst.) Geitl. can be utilized successfully in selective removal of toxic metal ions from metal contaminated or other kind of wastewaters. The results showed that immobilized cells could be repeatedly used in the sorption process up to five times. The rapid basification of algae-solution system enhances the cadmium uptake process.
Modelling metal uptake on a chelating resin: the case of Cd(II)/Chelex 100

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Ion exchange and complexing resins have found a large number of applications in many fields of biology and analytical chemistry; among them, the study of metal speciation and the development of sensors and samplers for in-field analysis, such as the DGT (Diffusive Gradients in Thin films) device. Despite their importance, only few experimental and modelling studies addressing the kinetics of metal uptake on chelating resins have been reported in the literature [1], and thorough studies on the effects of pH and ionic strength are needed.

A mixed control mass transport model (MiCoMo) that includes explicitly both particle and film diffusion steps has been developed; an accurate approximate analytical expression of this model was found, which has been successfully validated against the exact numerical solution. The model was applied to experimental data of Cd(II) uptake on Chelex 100, a widely used chelating resin. The influence of pH, ionic strength, stirring rate and initial metal concentration on the sorption dynamics were studied in batch experiments using a Cd Ion Selective Electrodes (Cd-ISE) for a continuous monitoring of the Cd(II) concentration in solution. Compared with periodic subsampling and off-line analysis with ICP-MS, ISE potentiometry proves to be a precise method, particularly useful in the case of fast uptake kinetics, when a high temporal resolution of the data is required.

Results show that MiCoMo can accurately fit the data and it successfully accounts for the influence of all the considered variables with a minimum number of constrained fitting parameters. The internal diffusion coefficient shows a remarkable inverse correlation with the resin/solution partition coefficient at equilibrium. The values of the latter coefficient as a function of pH and ionic strength were estimated from the Gibbs-Donnan model [2]. Particularly relevant is the model’s ability to predict the effects of the ionic strength on the uptake rate. The ionic strength is a variable of particular environmental interest whose role in the case of the DGT devices has been the object of thorough experimental and theoretical studies [3].

References
Efficiency of the bicarbonate activated peroxide system in the mild oxidation of phenolic dyes in aqueous and micellar solutions

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Introduction - In this study it was found that the generation of the nitrite anion during the oxidation of different phenolic dyes (indigo carmine, Congo red and crystal violet) greatly increases the oxidation rate of these compounds by the bicarbonate-activated peroxide (BAP) system in mild conditions. High nitrite/BAP molar ratios prevented the formation of polymeric species and favoured the degradation to aliphatic fragments. Indirect evidence suggested in situ generation of reactive oxygen species (ROS) such as peroxynitrite and nitrosoperoxyarbonate which may account the synergistic action of nitrite/BAP system. In addition, the effect of an anionic (sodium dodecyl sulfate), cationic (hexadecylpyridinium chloride) and nonionic surfactant (Triton X100) was investigated at concentrations below and above critical micellar concentrations.

The results can be exploited for developing environmental-friendly and cost-effective methods for the removal of phenolic dyes as alternative to current advanced oxidation processes.

Methods - The oxidations were conducted directly in the spectrophotometer cuvette, at constant temperature (25°C), by following the UV-VIS spectra in time until the dye was . The reaction was initialized by adding different volumes of H\textsubscript{2}O\textsubscript{2} stock solution such as the total H\textsubscript{2}O\textsubscript{2} concentration in the reaction mixtures ranged from 1\cdot10\textsuperscript{-3} to 3\cdot10\textsuperscript{-1} M. In all assays at least a 100-fold excess of bicarbonate was ensured with respect to the dyes. The interactions of dyes with surfactants were studied by recording the absorption spectra of 1 \times 10\textsuperscript{-5} mol L\textsuperscript{-1} dye solution containing surfactants in the concentration range from 1 \times 10\textsuperscript{-6} mol L\textsuperscript{-1} to 3 \times 10\textsuperscript{-2} mol L\textsuperscript{-1}. Binding constants and micelle/water partition coefficients for dye-surfactant system were determined from the absorbance changes occurred as a result of the interaction between dye and surfactant molecules.

Results - The calibration plots from colorimetric analyses were built up to calculate and eventually compare the conversion of substrates. The oxidant systems containing up to 10\textsuperscript{4} fold excesses of BAP for all dyes (indigo carmine, Congo red and crystal violet) yielded significant changes of conversion. The half-lives of the phenolic dyes (\(\tau_{1/2}\)) were calculated with respect to substrate/BAP molar ratio. A kinetic model describing the influence of surfactant on reaction rate was developed. The results are discussed on the basis of electrostatic and hydrophobic interactions between the kinetic micelles and malachite green.

Conclusions - We attempted to demonstrate that BAP system in tandem with aromatic dyes can provide a feasible in situ “self-destroying” technology of stable dyes in natural and waste water amenable for batch reactors. The bicarbonate anion, which is the main source of carbonate radical regenerates during the oxidation cycles and, as long as a stationary concentration of H\textsubscript{2}O\textsubscript{2} is ensured, the system can be implemented and developed along other AOP technologies for the removal of phenolic dyes.

Acknowledgement - This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI UEFISCDI, project number PN-II-PT-PCCA-2011-3.1-0031".
Oxidation of organic compounds with thermally activated pyroelectric materials

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In the light of stricter regulations concerning the occurrence of micropollutants in the water cycle, there is an ongoing search for new methods like advanced oxidation processes (AOP). These AOP should be able to degrade organic micropollutants like pharmaceuticals and pesticides efficiently at low costs. Within this search, the pyroelectric effect of ferroelectric materials was investigated.¹²⁴ Thereby, pyroelectric materials are thermally excited in an aqueous medium, where the subsequently generated charges on the surface of the pyroelectric material induce an electrochemical oxidation of organic compounds. Within this so-called pyro(electro)catalysis, the precursor 2′,7′-dichlorodihydrofluorescin (DCFH) was oxidized to the fluorescent dye 2′,7′-dichlorofluorescin (DCF) in the presence of different pyroelectric materials.¹² It was also possible to disinfect a solution of Escherichia coli bacteria and to hydroxylate coumarin to 7-hydroxycoumarin.¹³ Additionally, ESR-studies and the coumarin dosimetry confirmed that reactive hydroxyl-radicals (·OH) are generated during the thermal excitation of pyroelectric BaTiO₃.³

Besides these fundamental findings regarding the existence of a pyro(electro)catalytic process only little is known about the influencing reaction parameters (pH, thermal excitation, electrolyte,…) or the exact mechanism. Moreover, the effects of material parameters like the particle size/shape/porosity/surface, the pyroelectric constant or the crystallographic phase which could have an influence on the pyro(electro)catalytic oxidation process are still vague. The knowledge concerning these parameters is essential in order to design and synthesize corresponding pyroelectric catalysts and optimize the reaction parameters.

Within this contribution, new aspects of pyro(electro)catalysis will be presented in order to overcome parts of the above-mentioned knowledge gap. With the help of a modified DCHF-oxidation assay (scheme 1), the salicylic acid dosimetry and the coumarin dosimetry several reaction parameters, the excitation process and different pyroelectric materials like LiTaO₃, LiNbO₃ and BaTiO₃ will be contrasted in a comparable manner. With these methods, the overall oxidation capability as well as the amount of generated ·OH can be determined and will give an insight into the reaction mechanisms involved. As shown in Figure 1, the oxidation of DCHF could be increased significantly in the presence of LiTaO₃ by an alternating temperature field.[²]

![Scheme 1: Pyro(electro)catalytic oxidation of non-fluorescent DCHF to the fluorescent dye DCF.](image1)

![Figure 1: Comparison of a reference experiment (only thermally cycled 1 µM DCHF reaction solution) and two experiments with additionally added artificial matrix or LiTaO₃ powder.[²](image2)

References

Quantitative Adhesion of different bacteria with sesame seeds and oil extracts

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Sesame seeds are important oil seeds crops to humankind which contains diverse bioactive components including tocopherols, phytosterols, polyphenols and flavonoids [1]. Extracts from sesame seeds and oil have been used as fungicides and stabilizer in canned food for their ability to possess higher oxidative stability and also a great antifungal and antibacterial activity.

Our aim was to study the effects of the majority compounds of sesame extracts on the formation of biofilms on polyester, the adhesion experiments of different bacteria were carried out on different extracts at various contact time. The results were unexpected for all bacteria in all the contact times, the sesame extracts have no anti adhesive effect on bacteria, on the contrary, the extracts have a very remarkable adhesive effect over time for all bacteria, which proved that the compounds of sesame accelerated and increased the adhesion, and the level of this development depend on contact time.

This research suggests that it is very important to take into account the value of using sesame extracts as growth agents for beneficial bacteria.

Key words : sesame, adhesion, bacteria.

References :
Interfaces in nuclear waste disposals: experimental studies and modelling approaches

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Nuclear waste repositories include a range of engineering materials (steel, concrete …) that are emplaced deep into a rock formation. This means that strong chemical gradients are likely to occur at the contacts between different materials and at the interfaces between the engineered structures and the host rock.

At present, most of the performance storage concepts include a good number of interfaces such as metal-concrete, metal-clay, clay-concrete and engineered structures - host rock. In addition, interfaces including biotic and abiotic environments should be also taken into account. It is now generally acknowledged that microbes can survive even under extreme environmental conditions with a growth rate controlled by the availability of water, nutrients and energy sources.

Over the long timescales considered, solute transport processes will cause the locations of strong chemical gradients, forming reaction fronts. In this work we present three different examples focusing on redox and chemical gradients foreseen in the nuclear waste disposal after closure. At that time, water will saturate the engineered environment and could trigger simultaneously different processes, such as i) the release of organic compounds and salts, ii) metal corrosion reactions with H₂ production, iii) microbial activity, iv) strong pH and Eh gradients. The key biotic and abiotic processes expected at the interfaces and fronts will be discussed with special emphasis on the implementation of quantitative models based on static and dynamics experiments.

The first example focuses on the interface geosphere-near field, making a clear reference to the evolution of the hydrochemical conditions and the further impact on the long-term performance of engineered barriers. In this sense, the model provides predictions of the geochemical conditions in a rock volume that surrounds the facility and interfaces with the engineered barriers [1].

The second case study is based on the release of salts and organic compounds from the wastes and the expected impact on the clay and concrete barriers. The high-pH front resulting from the leaching of concrete barriers is particularly relevant as well as redox fronts controlled by biotic and abiotic reactions [2].

The last example describes the impact of H₂ generation by anoxic corrosion of metallic components. The presence of H₂ is able to modify the pH/Eh conditions, catalyses nitrate/sulphate reduction and provides a source of energy for microbes. All this processes will be analysed and discussed making reference to the experimental studies integrated in the geochemical models [3].

References


Impact of organic molecules on the colloidal stability of silica nanoparticles at environmental conditions

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The use of engineered metal (oxide) nanoparticles in a variety of applications and products is rapidly increasing. Among engineered nanoparticles, silica nanoparticles (often referred to as colloidal silica) is by far the most common industrial product, with extensive use in drug production, paper making, paints and sealants etc. Silica nanoparticles are generally considered to be non-toxic, but details of their interaction with environmental organic material are scarce, especially considering the multitude of available surface modifications.

Interaction between nanoparticles and natural organic material will result in formation of a primary corona, which will change the physical and biological characteristics of the nanoparticles and affect their fate. However, the structure and dynamics of this corona are not well understood, as a molecular level description of the interfacial reactions is lacking. We aim to improve the situation by studying the interaction between engineered silica nanoparticles and a number of organic molecules, using a combination of classic wet chemical methods, microscopy, spectroscopy and molecular simulations.

The colloidal stability of nanoparticles mainly depends on the ionic strength, the surface charge and the presence of bridging ligands. We have measured the surface charging of commercial silica NPs at various conditions using potentiometric titrations while the particle aggregation in the presence of various organic ligands has been evaluated using dynamic light scattering (DLS) and small angle X-ray scattering (SAXS). Shown below are plots comparing the evolution of particle size over time for a system containing only silica NPs in a 1 mM NaCl solution with a system which also contained the ligand 3,4-dihydroxybenzoic acid. It is obvious that the presence of this organic molecule strongly promotes particle aggregation at acidic conditions, while it appears to have minor or no effect at near-neutral conditions.

Figure 1 a,b: Measured sizes of Bindzil 40/130 silica nanoparticles versus time, with and without organic molecules present. The effect of the organic ligand on particle aggregation is obvious.
Utilization of Talaromyces sp. Isolated from Arsenic-Contaminated Mine Soil as an Efficient Biosorbent for Arsenic Removal

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Arsenic contamination of soil and natural water has been emerging as an important environmental issue since it poses significant health risks to millions of people worldwide. In particular, the chronic arsenic poisoning due to drinking untreated groundwater can be associated with adverse health effects such as skin cancer, and calls for emergent actions. Accordingly, various technologies to remediate arsenic-polluted soil and water have been developed for decades. Bioremediation is one of effective ways for arsenic removal from arsenic-contaminated media because it is environmentally benign and cost-effective process. In this study, we isolated hyper-tolerant fungal strains against arsenic and utilized them for the removal of arsenic as an efficient biosorbent. The arsenic-contaminated mine soil was screened by using solid and liquid culture media to isolate the culturable arsenic-tolerant microorganism and the only single culturable fungal strain was obtained. The fungus isolated was identified as Talaromyces sp. by PCR-based ITS1/ITS4 primers sets. Arsenic tolerance test on potato dextrose solid or liquid medium spiked with arsenic ranging from 25 to 1,000 mg/L revealed that the fungus was highly resistant to arsenic and tolerated arsenic up to 1,000 mg/L. However, the mycelial growth was slightly reduced and the sporulation pattern was changed with increasing arsenic concentration. In potato dextrose broth with arsenic (As(III), As(V)), a robust mycelial growth was observed in both cases. There was no difference of growth between control and arsenic amended cultures (up to 300 mg/L) for both arsenic species, while the mycelial growth was decreased to 20~42% with increasing the arsenic concentration over 300 mg/L. In case of biosorption of arsenic onto mycelial biomass, both As species were effectively removed from aqueous medium (>70%). Surface modification with iron oxides on the biomass significantly enhanced arsenic removal efficiency. The arsenic tolerance and removal mechanism of this strain was also proposed.
Contribution of particle penetration into DGT devices to the effective accumulation of Zn ions released in ZnO nanoparticle dispersions.

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Diffusion Gradients in Thin films (DGT) is increasingly been used in combination with ecotoxicological studies to assess the fraction of dissolved metal species released from metal and metal oxide nanoparticles (NPs) to the aqueous environment [1-3]. In this context, the evaluation of the DGT technique performance with NP dispersions and, particularly, the possible effect of partial penetration of the NPs into the diffusion gel, seems most timely and relevant. Here, a simple reaction-diffusion scheme is presented, which accounts for the diffusion of ZnO NPs into the DGT device and its subsequent dissolution within the hydrogel. The theoretical contribution of the internalized NPs to the overall Zn accumulation by the resin is evaluated as a function of several environmental and operational variables such as pH, particle size and bulk concentration, polydispersity or ZnO adsorption on the filter membrane. Experimental results obtained through DGT experiments with different device configurations are here compared with measurements carried out using AGNES [4].

The model calculations suggest that DGT measurements may overestimate the soluble fraction of ZnO NPs to a variable extent depending on pH and NP/free metal concentration ratios in the bulk solution. However, at relatively low pH values (7.5) and NP concentrations (below 100 mg·L⁻¹), the deviations in the theoretical accumulations from a situation in which NP penetration is absent are expected to be negligible. In these conditions, DGT should (at least theoretically) reflect the increase in the bulk solubility as the NP size decreases, as predicted by the Ostwald-Freundlich theory. The large uncertainty associated to the diffusion coefficients of the particles in the gel is acknowledged, and, thus, homogeneity of the gel structure within each device, as well as consistency among gel batches, is critical for a reproducible performance of DGT experiments.

References

Acknowledgements - The authors thank support from European Union Seventh Framework Programme (FP7-NMP.2012.1.3-3) under grant agreement no. 310584 (NANO+REG), and from the Spanish Ministry of Education and Science (Projects CTM2012-39183 and CTM2013-48967).
Chemical modifications on pinus bark for adsorption of toxic metals

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Pollution of surface and underground water is a worldwide problem. Among the several sources of pollution, water contamination by toxic metals is one of the most serious since these metals present a high degree of toxicity to humans and to the environment, even at low concentrations. This way, the current research produced modified adsorbents from pinus bark with high removal capacity of Cd(II), Pb(II) and Cr(III) from water. Pinus bark was obtained directly from pinus logs and the biomass was chemically modified by solutions of H2O2, H2SO4 and NaOH 0.1 mol L-1. Was evaluated the relationship between pH of Cd, Pb and Cr solutions and adsorbent masses as well as the effect of contact time, equilibrium and thermodynamics. In Table 1 are presented results for adsorption kinetics for pinus modified adsorbents.

<table>
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<tr>
<th>Parameters / Adsorbents</th>
<th>P. H2O2</th>
<th>P. H2SO4</th>
<th>P. NaOH</th>
<th>P. H2O2</th>
<th>P. H2SO4</th>
<th>P. NaOH</th>
<th>P. H2O2</th>
<th>P. H2SO4</th>
<th>P. NaOH</th>
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<td>-0.00932</td>
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<tr>
<td>Qe (cal.) (mg g^-1)</td>
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<td>0.870</td>
<td>0.901</td>
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Table 1. Kinetic parameters for removal of metals Cd(II), Pb(II) and Cr(III) by modified adsorbents of pinus

<table>
<thead>
<tr>
<th>Adsorbents</th>
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<th>Cd</th>
<th>Pb</th>
<th>Cr</th>
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<td>P. H2O2</td>
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<td>C_i (mg g^-1)</td>
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<td>R2</td>
<td>0.125</td>
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<tr>
<td>P. H2SO4</td>
<td>Kd (g mg^-1 min^-1/2)</td>
<td>0.00869</td>
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<td>C_i (mg g^-1)</td>
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</tr>
<tr>
<td></td>
<td>R2</td>
<td>0.431</td>
<td>0.922</td>
<td>x</td>
</tr>
<tr>
<td>P. NaOH</td>
<td>Kd (g mg^-1 min^-1/2)</td>
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<td>0.0311</td>
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<td></td>
<td>C_i (mg g^-1)</td>
<td>2.42144</td>
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<tr>
<td></td>
<td>R2</td>
<td>0.381</td>
<td>0.946</td>
<td>0.984</td>
</tr>
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</table>

K1: constant of pseudo-first order rate; Qe: amount of adsorbate retained by adsorbent gram in equilibrium; Kd: constant of pseudo-second order rate; a: constant indicating chemisorption initial rate; b: number of suitable sites for the adsorption of the surface related to coverage extension and the activation energy of chemisorption; C_i: suggests thickness of the boundary layer effect; R2: coefficient of determination.

The model of pseudo-second order shows high R2 rates and calculated Qe (Qe_calc) rates very close to experimental results (Qe_exp), the adsorption process seem to be chemical, in other words, suggesting chemisorption of Cd(II), Pb(II) and Cr(III). The models of pseudo-first order, Elovich and intraparticle diffusion did not presented satisfactory adjustents for the adsorption process of Cd(II), Pb(II) and Cr(III). Studies evolving the pH of mean and adsorbent masses indicate that the evaluated pH range (3.0 to 7.0) did not influence the adsorption process, being this a great advantage for the use of these materials for different pH water conditions. The data obtained for isotherms construction show an increase in the capacity of adsorption for Cd, Pb and Cr of 413 (Qm of Langmuir), 259 (Qe of Langmuir) and 207% (Kf of Freundlich) for P. NaOH, P. NaOH and P. H2SO4, respectively. The modifying solutions were effective in increasin the capacity of metals adsorption of pinus barks. These results indicate that pinus modified with alcaline, acid or oxidants produced higher adsorption capacity, in monolayer and multilayer sorption of Cd(II), Pb(II) and Cr(III).

Acknowledgement - The authors would like to thank the CNPq for its funding and research productivity and the CAPES for the postgraduate scholarship.
Preparation of activated carbon from birch polypore for CO$_2$ adsorption

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The global energy system is based largely on fossil fuels. These fuels are responsible for about 1/3 of all CO$_2$ emissions. This emission is linked to the global energy demand and steadily rising. It is therefore important to try to stabilize the concentration of CO$_2$ in the atmosphere. Although important measures are being taken, such as increasing the share of renewables or improving the efficiency of energy conversion processes, it is widely accepted that Carbon Dioxide Capture and Storage, will be necessary if the demand for energy is will be increase, without contributing to global warming in the forthcoming years. One solution is the use of adsorbent in the form of activated carbon. Activated carbons present a series of advantages With as CO$_2$ adsorbents, among other things: a high adsorption, ease of regeneration, low cost production [1,2,3]. The aim of the study was to evaluate the properties of activated carbons obtained from the birch polypore treated by potassium hydroxide.

Birch polypore were us as a carbon source. Activated carbons synthesis: impregnation by dry KOH during 3 h (dry mass ratio KOH: carbon source = 1:1), drying at 200°C, carbonisation for 1h, under nitrogen at 700-900°C, washing with distilled water, treating with 1 M HCl for 19 h, washing with distilled water until neutral, drying at 120°C. The specific surface area ($S_{BET}$), a total pore volume ($V_p$), and micropore volume ($V_{mic}$) were estimated by nitrogen sorption at a temperature of -196.15 °C. CO$_2$ adsorption was measured by volumetric method.

Textural properties values are shown in Table 1. The highest specific surface area: 2399 m$^2$/g, the largest total pore volume ($V_p$): 1.57 cm$^3$/g and micropore volume ($V_{mic}$): 0.71 cm$^3$/g were obtained at 900°C. The largest adsorption of CO$_2$ was observed at 0°C on activated carbon prepared at 900°C and amounted to 5.15 mmol/g. The largest adsorption of CO$_2$ at 25°C was observed on activated carbon obtained at 700°C and amounted to 5.50 mmol/g.

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>BET m$^2$/g</th>
<th>$V_p$ [cm$^3$/g]</th>
<th>$V_{mic}$ [cm$^3$/g]</th>
<th>CO$_2$ adsorption at 0°C [mmol/g]</th>
<th>CO$_2$ adsorption at 25°C [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H700</td>
<td>1347</td>
<td>0.57</td>
<td>0.49</td>
<td>5.41</td>
<td>5.50</td>
</tr>
<tr>
<td>H750</td>
<td>1155</td>
<td>0.55</td>
<td>0.41</td>
<td>4.65</td>
<td>4.88</td>
</tr>
<tr>
<td>H850</td>
<td>1336</td>
<td>0.58</td>
<td>0.49</td>
<td>5.03</td>
<td>4.62</td>
</tr>
<tr>
<td>H900</td>
<td>2399</td>
<td>1.57</td>
<td>0.71</td>
<td>5.15</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Table 1. The values of specific surface area, pore volume, micropore volume and adsorption at 0°C and 25°C

The present study shows that the carbon from birch polypore is an effective adsorbent for the carbon dioxide removal. Since the raw material fungus arboreal is freely available in large quantities in world activated carbon produced from birch polypore will be cheap.

References
Activated carbon from waste of carboxymethyl starch film as CO₂ adsorbent

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The films obtained from the carboxymethyl starch have good mechanical properties and biodegradability. They are non-toxic, colorless, odorless and odorless. All substances used as the raw materials are renewable and relatively cheap.

In the production certain amount of the film becomes a waste. This valuable material is irreversibly lost. The waste of carboxymethyl starch film can be utilized as raw material for activated carbon production. According to our knowledge such utilization of carboxymethyl starch film waste was not described. Obtained activated carbon can be used as CO₂ sorbent.

Carboxymethyl starch film was used as a carbon source. Dry KOH was utilized as activating agent. The mass ratio KOH: carbon source was equal to 1:1. After activation mixtures were dried at 200°C and carbonized for 1h, under nitrogen at 500-700°C. Then samples were washed with distilled water, treated with 1 M HCl for 19 h, washed with distilled water until neutral and dried. The specific surface area (S_BET), a total pore volume (V_p), and micropore volume V(mic) were estimated by nitrogen sorption at a temperature of -196.15 °C. The adsorption of CO₂ on activated carbons at a pressure of 1 bar at 0°C were investigated by volumetric method. These values are shown in Table 1.

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>S_BET [m²/g]</th>
<th>V_p [cm³/g]</th>
<th>V_mic [cm³/g]</th>
<th>CO₂ adsorption at 0°C [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2064</td>
<td>1.19</td>
<td>0.67</td>
<td>4.48</td>
<td></td>
</tr>
<tr>
<td>CMS550</td>
<td>443</td>
<td>0.22</td>
<td>0.17</td>
<td>2.97</td>
</tr>
<tr>
<td>CMS600</td>
<td>743</td>
<td>0.38</td>
<td>0.26</td>
<td>4.49</td>
</tr>
<tr>
<td>CMS700</td>
<td>847</td>
<td>0.41</td>
<td>0.31</td>
<td>2.82</td>
</tr>
</tbody>
</table>

Table 1 The values of specific surface area, total pore volume and micropore volume of obtained activated carbon

The highest surface area, total pore volume (V_p) and micropore volume was noticed for CMS500. The highest adsorption of CO₂ was observed on activated carbon produced at 600°C and was equal to 4.49 mmol/g. This work showed that carboxymethyl starch can be used as the good raw material for the production of activated carbon.
Carbonaceous catalyst from orange pulp for limonene oxidation

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Limonene can be obtained from orange peels by simple distillation. Orange peels are waste from the fruit juice industry. Limonene is the very important raw material for 1,2-epoxylimonene, 1,2-epoxylimonene diol, perillyl alcohol, carvone, and carvone synthesis. These products are valuable intermediates for the production of food flavorings, perfumes, cosmetics, drugs, pesticides and polymers. The very valuable waste after limonene distillation is the orange pulp. We demonstrate here the utilization of this orange pulp as the raw material for the carbonaceous materials that can be catalysts for limonene oxidation.

The orange pulp from orange peels after distillation was used as the raw material. Dry pulp was wetted with H₂O, then was added silicon balls prepared by Stöber method (KSi). Three samples were prepared. The first sample obtained by mixing with dry sodium hydroxide (OPNa) and the second with potassium hydroxide (OPK). The third sample (OP) was prepared without any additives. Each samples were dried for 2h at 60°C then 16h at 160°C. Pyrolysis was conducted in a horizontal tube furnace at 750°C for 1h under nitrogen atmosphere. Then the samples were soaked with 10 wt% HF acid. Samples were washed by distilled water until filtrate was neutral.

The oxidations of limonene were carried out in methanol and at the raised temperatures. The H₂O₂ and TBHP were used as oxidants. The limonene: oxidant molar ratio was equal to 1:2. The process was carried out in a glass reactor, equipped with a reflux condenser, a thermometer and a magnetic stirrer. Samples taken at different reaction time were analysed by a GC-method on a Focus apparatus equipped with a flame-ionization detector.

The XRD method confirmed that carbonaceous material were obtained. Two broad peaks typical for turbostatic carbon were observed. Because silicon balls very unique material was obtained. The morphology of OP is presented at the Fig. 1.

![Fig. 1 The SEM picture of OP material](image)

We found that carbonaceous catalysts obtained from orange pulp are good catalyst for limonene oxidation. During the oxidation process the following products were obtained: carvone, carvone, perillyl alcohol and diol of 1,2-epoxylimonene.
Preparation of activated carbon from common polypody for $H_2$ adsorption

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Hydrogen is considered to be the cleanest fuel and will be able to revolutionize the transport and energy market. Hydrogen can be the real alternative for fossil fuel. The main benefits are its low density and small volume heat of combustion. But recently none of the existing methods of hydrogen storage is efficient. It is important to find the most effective way to store hydrogen. Now the research have focused in the search of the high capacity adsorbent to hydrogen. Activated carbons is perspective candidate for hydrogen adsorption storage. The aim of the research was to produce and use activated carbon from common polypody for hydrogen adsorption. According to our knowledge such application for common polypody was not described up to now.

Common polypody was us as a carbon source. Activated carbons synthesis is shown on figure 1. The various temperature of pyrolysis was equal to 700, 800 and 900 °C.

XRD analysis confirmed that activated carbons were obtained. High pressure $H_2$ adsorption studies were performed using Sievert’s apparatus – Hiden Isochema Intelligent Manometric Instrument (IMI). The samples were degased in the IMI before the measurements at 260°C under vacuum for 16 h. The $H_2$ adsorption isotherms were measured at the temperature of 40°C The equation of state was used to calculate the amounts of adsorbed $H_2$. The results of hydrogen adsorption shown on figure 2

The results of hydrogen adsorption are shown at figure 2. Samples values at 40 bar. The adsorption of hydrogen at activated carbon obtained at the temperatures 800 and 900 °C were similar but the highest was at P800. At the pressure of 40 bar hydrogen adsorption was equal to 4.1 mmol/g.

Activated carbons obtained from common polypody can be good hydrogen storage materials.
Enhanced removal and degradation of an organophosphate insecticide by acid-activated polymer-clay composite surfaces

Itamar Shabtai and Yael Mishael

Diazinon is an organophosphate insecticide widely used in agriculture and often detected in surface and groundwaters. Diazinon is moderately stable in neutral pH but undergoes rapid hydrolysis in alkaline and acidic pHs. The major byproduct of diazinon hydrolysis, 2-Isopropyl-6-methyl-4-pyrimidinol (IMP), is much less toxic. In the current study, a montmorillonite-based poly-vinyl pyridine composite (PVP-MMT) was acid activated (HPVP-MMT) and employed as a bifunctional sorbent, for the adsorption and surface catalyzed hydrolysis of diazinon. Batch adsorption experiments were carried out to determine the effect of composite acid-activation on sorbent capacity, diazinon adsorption affinity and surface induced hydrolysis. Diazinon adsorption by the bare clay was moderate (as reported in the literature) due to interactions of the phosphoric group with exchangeable cations of the clay, explaining the extremely low affinity of IMP (which lacks this group) to the clay surface. The adsorption of IMP and of diazinon was enhanced by acid activating the composite surface and it increased as a function of HPVP loading on clay, reaching 95% of the diazinon, for 0.06 g HPVP/g clay. Higher loadings (up to 0.13 g HPVP/g clay) gave rise to surface charge reversal (positive zeta potentials) but did not further enhance adsorption, suggesting electrostatic interactions were not a significant adsorption mechanism. The high affinity of diazinon and IMP to the HPVP-MMT surface may be attributed to H-bonding. H-bonding between the pyrimidinol moiety of diazinon and IMP and the protonated pyridine was supported by composite column filtration experiments of diazinon, from an acidic and neutral solutions. Diazinon filtration (120 pore volumes) by the composite column from an acid and neutral solution was high and low, respectively. Subsequent to diazinon filtration, the column was regenerated by passing an alkaline solution (60 pore volumes). The elution of the column subjected to acidic pH was more efficient (100%) than that of the column subjected to neutral pH (47%) indicating the feasibility of facile regeneration of the composite. Supporting surface enhanced catalysis, the amount of IMP eluted was significantly higher than initially adsorbed (from the column subjected to acidic conditions). Finally, adsorption kinetics of diazinon and IMP was significantly faster by HPVP-MMT than by granular activated carbon (GAC). The high binding capacity and affinity, surface enhancing hydrolysis capabilities, superior adsorption kinetics and composite regenerability indicate that HPVP-MMT may be successfully employed for treatment of diazinon contaminated waters.
Sorption of aromatic organic acids to biochar

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The remediation of sites diffusely contaminated at low concentrations can be cost intense and is therefore often not cost effective, but untreated sites may nevertheless pose risks to both soil and groundwater resources. Biochar, a product of biomass pyrolysis, is used in agriculture to increase soil pH and water holding capacity and may have a positive effect on soil biota. Recently, the potential use of biochar to immobilize neutral organic contaminants and heavy metals showed promising results [1]. Hence, using biochar in remediation applications may help stabilize and renaturalize contaminated soils.

Many contaminants of concern and naturally occurring infochemicals, are organic acids that dissociate under environmental conditions, and may thus exist as neutral and/or anionic species. The sorption of dissociated organic acids to biochar, is typically lower than that of neutral species, but is driven by complex processes that are not yet fully understood. Approaches to predict sorption developed for neutral compounds and based on Kow, are unlikely to be suitable for organic acids, due to the effects of dissociation on sorption. Previous studies on the sorption of organic acids to soils have demonstrated that Dow, which describes the decrease in hydrophobicity of acids as a result of dissociation, is a useful alternative to Kow [2].

The aim of the present study was to test the applicability of a Dow based concept to describe the sorption of organic acids to biochar and other carbonaceous sorbents. Batch experiments were performed with a series of materials including a variety of biochars, carbon nanotubes, and activated carbon, and four acidic compounds commonly used for pesticidal and biocidal purposes (i.e., 2,4-D, MCPA, 2,4-DB, and triclosan). The wide range of properties considered allows discussing (i) the mechanisms driving the sorption of neutral and anionic species to biochar, and (ii) their dependency on sorbate and sorbent properties.

Results showed that the sorption of the four acids was influenced by factors that are usually not considered for neutral compounds. Dissociation affected the sorption of the four organic acids, and sorption of the anions ranged over five orders of magnitude, thus substantially contributing to sorption in some cases. For prediction purposes, most of the variation in sorption (89%) could be well described with a two-parameter regression equation including Dow and N2 BET surface area [3]. The proposed model may serve as a base to estimate the environmental fate of organic acids in the presence of biochar.

References:


The effects of ionic silver and nanosilver on cell membranes of two Gram-negative bacteria: *Escherichia coli* and *Pseudomonas aeruginosa*

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Bacteria are unicellular organisms abundant in soil and water but also in the human body. Although bacteria are crucial in biogeochemical cycles in the environment, some bacteria such as e.g., *Escherichia coli* and *Pseudomonas aeruginosa* can also cause health problems. To prevent or fight these conditions, various types of antimicrobials are used, whereas silver nanoparticles (nAg) are one of the most promising antimicrobial compounds. Despite numerous studies, the antimicrobial mechanism of nAg is still under debate. It is generally accepted that antibacterial properties of Ag are dictated by their dissolved fraction. However, dissolution-based concept alone does not fully explain the toxic potency of nanoparticulate silver compared to silver ions. We have previously shown that different bacterial strains exhibit similar susceptibility to AgNO₃ but not to nAg, whereas the toxicity of nAg to different bacterial strains, incl. E. coli and P. aeruginosa, remarkably varied, assumingly due to differences in cell-nAg interface and cell membranes [1].

The main aim of this study was to investigate the effects of Ag ion (AgNO₃) and nAg-Col (Collargol, a protein coated nAg) on bacterial membranes in more detail and compare the membrane-related mechanisms of toxicity between two Gram-negative bacteria, *E. coli* and *P. aeruginosa*, that have two cellular membranes: inner and outer membrane. We used recombinant bacterial strains that emitted light when viable. In addition to AgNO₃ and nAg-Col, polymyxin B (PMB; an antibiotic permeabilizing cell membrane) and membrane-penetrating organic compound 3,5-dichlorophenol (3,5-DCP) were included as positive controls. The effects of silver compounds on bacterial cell membranes were studied using different approaches: (i) kinetic bacterial bioluminescence inhibition assay that allows quick (seconds) estimation of bacterial membrane damage and associated loss in energy production; (ii) viability test based on bacterial colony forming ability after exposure to toxic compounds; (iii) flow cytometry to assess bacteria-NP interaction and possible uptake of nAg; (iv) staining of the cells with 1-N-phenylnaphthylamine (1-NPN) to estimate the possible permeability changes induced in outer membrane and (v) tetraphenylphosphonium (TPP) assay to discriminate the effect of toxicants on bacterial inner and outer membranes. In addition, dissolution of nAg in test conditions was quantified.

10-min bacterial bioluminescence inhibition assay and 1-h viability test showed that Ag ions and nAg-Col had rapid effects on cell membranes and viability. *P. aeruginosa* was more susceptible to Ag ions and nAg-Col (1-h minimal bactericidal concentration, MBC, values: 10 μM AgNO₃; 40 μM nAg-Col) than *E. coli* (80 μM AgNO₃; 320 μM nAg-Col), whereas *E. coli* was more susceptible to antibiotic PMB. In bioluminescence inhibition assays, the 10-min half effective concentration (EC50) values (in μM) for Ag-ion and nAg-Col were 5.7 and 21.4 for *E. coli* and 2.3 and 7.7 for *P. aeruginosa*, respectively. The differences in toxicity of Ag-ions and collargol in both toxicity tests were explained by solubilised Ag-ions, as the dissolution of nAg-Col in the test medium was ca 30%. However, flow cytometry analysis showed specific interactions of nAg-Col with *P. aeruginosa* cells, different from these observed for *E. coli*. TPP assay showed that the Ag compounds (5 μM Ag ion; 160 μM Collargol) rapidly (in 10 min) depolarized bacterial inner membrane but did not permeabilize the outer membrane of neither bacteria. The latter was confirmed by 1-NPN staining. In conclusions, *P. aeruginosa* was more susceptible to Ag ion and nAg-Col compared to *E. coli*. The toxicity of nAg-Col to both bacteria was related to (i) dissolution and (ii) specific effects on the outer membrane of bacteria that was more pronounced in case of *P. aeruginosa*.

References

Acknowledgements. This research is supported by Estonian Ministry of Education and Research (target-financed theme IUT23-5 and PUT1015) and Lithuanian Research council (grant No MIP-040/2015).
CO₂ capture mechanism of Gamma-dicalcium silicate in cementitious materials

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One of the major challenges facing mankind since the start of the 21st Century is not only the ever deteriorating climatic conditions but the unpredictability of the weather as well. One of the industrial activities by mankind that lead to the increase in the carbon dioxide in the atmosphere is the manufacture of Ordinary Portland cement (OPC), a common binder in the construction and civil engineering industry. Carbon dioxide emissions from OPC production is about 7% of the total carbon dioxide emissions. Carbon dioxide capture is a means, mechanism or system of reducing the existing CO₂ concentrations in the atmosphere. The CO₂ capture systems have gained credence in mitigation of global warming therefore they are important to study and improve. One of these systems is the decrease in the quantity of OPC produced by blending it with other cementitious materials like fly ash and blast furnace slag. These materials are mostly freely available as wastes from industrial processes so blending them with OPC in the right proportions would decrease the amounts of OPC produced and thus reduce the CO₂ emissions from the cement industry and this reduction is further enhanced when they serve as active carbon capture materials. There is need to expand on the diversity and increase on the number of practical cementitious materials admixtures that can be blended with OPC. Gamma dicalcium silicate (γ-C₂S) is a candidate cementitious material that could also serve the purpose of CO₂ capture. This study therefore seeks to evaluate the viability of formulating composite blends of OPC and γ-C₂S, to study their mechanical properties of resulting mortars and pastes as regards the requisite engineering standards, and how these composite blends can serve as a carbon dioxide capture tool to mitigate the phenomenon of global warming. The carbonation of OPC as given above reduces the CO₂ in the atmosphere. This capture was demonstrated in the work that developed a new ecological concrete based on special admixtures of gamma phase dicalcium silicate (γ-C₂S) that could achieve a CO₂ emission level from a thermal power station below zero by reacting with CO₂ and hardening in the process [Yoshiaka I. et al, 2013]. The quantity of CO₂ emitted with this material was reported to be one—fifth of that of OPC concrete. Separate work also related to γ-C₂S had been carried out that proved that carbonates were formed from CO₂ and the mixture of OPC and other mineral admixtures like γ-C₂S and Low Heat Portland cement [Watanabe K. et al, 2006]. This means that OPC mortars, especially those whose admixtures like γ-C₂S have the ability to capture CO₂ from the environment.

In this study, we used synthesized Gamma dicalcium silicate by using limestone sludge and waste foundry sands and waste Gamma dicalcium silicate from magnesium steel slag. And tested CO₂ diffusion in OPC and physical properties of hardened OPC. And so, we find that carbon dioxide reacts with OPC and/or its blends to form CaCO₃. This carbonate is deposited in the pore structure of the hardened OPC and in so doing reduces the volumes of the pores. The reduction of pore volume brings about a decrease in the porosity of the OPC and consequently reduces its permeability to CO₂. OPC formulated by substituting portions of OPC with γ-C₂S can capture CO₂ from the atmosphere.

References
Roles of interfaces in the UV-induced mineralization of terrigenous dissolved organic matter

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Land-water interfaces play important roles in the UV-induced mineralization of terrestrially derived dissolved organic matter (DOM). The reason is that terrigenous DOM (tDOM) generally exhibits a higher specific rate of light absorption than autochthonous DOM (derived from aquatic algal and bacterial biomass), attributed to the high aromaticity of the former. In aquatic ecosystems, UV-induced oxidation of tDOM produces CO₂ and this process is one of several mechanisms by which natural organic matter in aquatic and soil environments may play an important role in climate feedbacks. Climate change has led to changing hydroclimatic conditions in both the Northern and Southern Hemisphere, for example, to long-lasting heavy precipitation events. Furthermore, global warming enhances the thawing of permafrost soils, particularly in the Arctic. Heavy precipitation events and, as a consequence, enhanced continental runoff and river discharge, as well as thawing of permafrost soils are likely to increase the net transfer of tDOM from land to surface waters. Dissolved organic matter draining from thawing permafrost soils is highly photoreactive and becomes bioreactive after exposure to sunlight. This phenomenon can be explained by increasing tDOM bioavailability via photochemical transformations of tDOM. Coupled photochemical and biological mineralization of DOM to produce CO₂ is expected to be an important process in the Arctic carbon cycle, as the Arctic continues to warm and as permafrost soils continue to thaw. The release of CO₂ from thawing permafrost soils in the Arctic has been proposed as a major positive feedback on global warming.

In addition to tDOM, also iron in the form of Fe(III)(hydr)oxides is transported from land to water. Heavy precipitation events can be expected to enhance the transfer of iron from iron-rich soils into surface waters. Heterogeneous iron photochemistry may catalyze or enable the UV-induced mineralization of photostable DOM. The release of CO₂ from thawing permafrost soils in the Arctic has been proposed as a major positive feedback on global warming.

This poster is based on a Critical Review by Sulzberger and Arey (2016)¹ and on a recent paper by Sulzberger (2015)². It will address the following questions: (i) How do polar changes affect hydroclimatic conditions in temperate regions? (ii) What are the mechanisms involved in the UV-induced mineralization of tDOM? (iii) What are the roles of iron in the UV-induced mineralization of photostable DOM? (iv) What type of research is needed to estimate the magnitude of potential feedbacks on climate caused by UV-induced mineralization of tDOM?

References
Effect of the tsunami (Chile, 2010) on Cd, Cr, Cu, Mn and Zn concentrations in the mollusc *Concholepas concholepas*

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Abstract

The Cd, Cr, Cu, Mn and Zn concentrations were measured in samples of *Concholepas concholepas* (Mollusca, Gastropoda) obtained in the coastal zone of Iloca, Maule Region, Chile. The mollusc *Concholepas concholepas*, known as “loco” in Chile, is endemic to the south-east Pacific with distribution from Lobos de Aforua Island (06°57’ S) in northern Peru to Cape Horn (55°52’ S) in southern Chile, including the Juan Fernández Island. The samples were collected during two periods, one before and one after the tsunami which occurred in the Maule Region, Chile, on 27 February 2010 as a result of an earthquake measuring 8.8 on the magnitude of moment scale (Mw).

The measurements were taken by atomic absorption spectroscopy in the hepatopancreas and muscle tissue of each specimen, considering shell-size (length and width). The method was validated using certified reference material. The concentration ranges determined in muscle tissue for January 2010 were: Cd: < 0.01 – 3.25; Cr: < 0.01 – 3.38; Cu: 0.39 – 62.69; Mn: 1.82 – 6.81 and Zn: 19.70 – 71.18 mg kg⁻¹ (dry weight). For October 2014, the ranges were Cd: < 0.01; Cr: 0.05 – 7.09; Cu: 1.42 – 47.34; Mn: 0.24 – 12.68 and Zn: 24.64 – 96.20 mg kg⁻¹ (dry weight). The concentrations in muscle tissue were generally lower than those found in the hepatopancreas of each specimen. The results for Cd, Cr and Zn in the edible part of the mollusc (muscle tissue) were within the ranges published for similar species however, the Cu and Mn levels were generally higher than reported in the literature. Nevertheless these values were below the maximum concentrations permitted under current legislation (FAO/WHO, 2004; EU, 2001) and do not constitute a health hazard for consumers. Statistical analysis showed that in the post-tsunami period Cr and Mn concentrations increased in muscle tissue and Cu, Cr and Mn concentrations increased in hepatopancreatic tissue. Analysis of correlation coefficients showed that the morphometry of the samples analysed did not influence the concentrations of metals in muscle and hepatopancreatic tissue.

**Keywords**: Heavy Metals, Maule Region, Tsunami, Mollusca.

**Acknowledgments**: The authors acknowledge support from Proyect PIEI: Química y Bio-orgánica en Recursos Naturales, University of Talca, Chile.
Heavy metals in industrial sludge: Occurrence, Leaching behavior and Environmental implications

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Industrial activities generate different types of waste, with varying chemical properties. An investigation of the detailed chemical and mineralogical characteristics of these materials may serve as a first step for selecting an appropriate treatment or safe disposal method. This study focuses on arsenic (As) and heavy metals (i.e., Cd, Co, Cu, Cr, Mo, Ni, Pb, and Zn) in three sludge samples derived from industrial wastewater treatment plants in Southern Vietnam. The emphasis is on determining the influence of changing environmental conditions on element mobilization based on a multidisciplinary approach using sample micro analysis (Field Emission Gun Electron Probe Micro Analysis (FEG-EPMA)) in combination with different types of leaching/extraction tests. Bulk chemical composition (ICP-OES measurement after digestion by 3 acids (HNO$_{3\text{conc}}$, HClO$_{4\text{conc}}$, and HF$_{\text{conc}}$)) showed a high variation of arsenic and heavy metals in the studied sludges: As (8-2410 mg/kg), Cd (0.4-2.0 mg/kg), Co (6-16 mg/kg), Cr (83-588 mg/kg), Cu (131-687 mg/kg), Mo (2-12 mg/kg), Ni (45-146 mg/kg), Pb (28-11347 mg/kg), and Zn (1324-33526 mg/kg). Micro-analysis by FEG-EPMA showed that most of the Zn-rich spots were found in association with S and Si-rich phases in Zn-rich sludge. Other heavy metals could not be detected except Pb (2 spots), that was found in Fe-rich phases in the Pb-rich sludge. In this study, besides the bulk chemical determination, a combination of extractions and leaching tests (i.e., pH-dependence leaching tests and ammonium-EDTA extraction) was used to assess a wide range of possible exposure conditions of the sludge and link it to potential management options. Although the leachability of most of the heavy metals decreased considerably at neutral and alkaline pH-conditions (pH 7-10), the leachable concentrations of arsenic and some heavy metals still exceeded the EU-leaching values for inert waste (As, Cr, Cu, Mo, and Pb) and for non-hazardous waste (As, Ni, and Zn) in some sludge samples.

![Figure 1: pH dependent leaching behavior of Zn in the Zn-rich sludge.](image)

Chelating agents, such as humic acids, can influence the leaching of heavy metals and arsenic. The potential complexation of heavy metals with chelating agents was assessed by mean of an ammonium-EDTA extraction. A textile dying sludge contained very high total Pb-concentrations (11347 mg/kg), which also showed a very high potential mobility, as 85% of the total Pb content was extracted with ammonium-EDTA. On the one hand, this result implies a threat to the environment, while on the other hand this indicates that washing with EDTA might be the first and efficient step to remediate and recover Pb from this kind of sludge. In the view of resource efficiency, landfilling, which is most often applied in Vietnam, is not a sustainable waste management option for this kind of sludge.
Azo-dyes degradation by covalently immobilized peroxidase onto epoxy-activated supports

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The colored wastewater treatment has been paid attention in the recent years due to the highest amount of dyes (about 15%), mostly carcinogenic, that are discharged into the water mainly due to the inefficacy of the dyeing processes [1].

Several approaches including physical, chemical, microbial and enzymatic treatments have been reported [2]. Among these methods, the enzymatic degradation shows advantages such as shorter processing time, reduction in sludge volume and ease of controlling the process. However, the enzymes solubility in water phases, high costs, low stability, has limited the applicability of oxidative enzymes for industrial purposes. A solution to improve the enzymes performances and operational stability is immobilization [3].

In this work different industrial dyes including Amido Black 10, Acid Red 1, and Acid Orange 7 were tested as substrates for horseradish peroxidase. The native enzyme was covalently immobilized onto two types of epoxy-supports, different in spacer length. The resulted biocatalyst has been in detail characterized in terms of pH, temperature stability and reusability.

Among the tested dyes the highest substrate conversions values (up to 98%) were obtained for Amido Black 10. The highest recovered activity was obtained when the EC-HFA, with the longest spacer arm sepabeads was used as support. After six reuses cycles for the degradation of Amido Black 10 dye, the covalently bound peroxidase preserved 70% of the initial activity.

References

Acknowledgement This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1319, and partially by Program 2 of the Institute of Chemistry Timisoara of Romanian Academy (Research Project 2.4.).
Removal of pharmaceuticals by clay-polymer sorbents: batch and filtration experiments.

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Significant concerns have been raised up due to the presence of organic micropollutants in surface waters. The ability of two polymer-clay sorbents (Tct-bent; Pnb-bent) based on a functionalized cationic starch was examined for the removal of three pharmaceuticals: atenolol (AT), sulfamethoxaxole (SMX) and diclofenac (DC). In batch experiments, the Tct-bent complex which exhibited a planar conformation of the polymer on the clay surface and higher cationic charge density showed higher sorption of DC and SMX over those of Pnb-bent but similar with AT. An analysis of the sorption by fitting to Langmuir equation showed a preferential sorption of DC over SMX on the polymer-clay complexes: lesser sorption sites (lower Ro) but more energetically favored (higher binding coefficient, K\textsubscript{L}). The sorption mechanisms of DC and SMX on Tct-bent were determined by thermal and infrared techniques: DC molecules formed an ion pair including hydrogen bonds through their secondary amine groups; SMX sorbed by strong electrostatic interactions followed by proton transfer involving its sulphon-nitrogen group and the hydroxyl moieties of the composite. Filtration experiments showed a better performance of the columns made of Tct-bent on DC and SMX over that of GAC (Figure 1). Accordingly, there are certain pollutants as those capable of protonation in solution (AT) that are sorbed on the developed hydrophobic domains of the polymer but in a smaller extension than GAC. Therefore, further studies should address the possibility of using mixed filters containing polymer-clay composites and GAC for a more efficient filtration. The filtration processes were successfully modeled by using an adsorption-convection model which enabled predictions under different operational conditions.

\textbf{Figure 1.} PhAcs filtration in columns including Tct-bent complex or GAC mixed with sand (2:100 w:w) at a flow velocity of 1.19 m/h.

\textbf{Acknowledgements} - This research was funded by the grant NANOWAT (ref. I-B/2.1/049) within the ENPI-CBC-MED programme of the European Union, and the Spanish Ministry of Economy and Competitiveness (project CTM2013-42306-R).
Biodegradation of Polycyclic Aromatic Hydrocarbons by Indigenous Microorganisms

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Polycyclic aromatic hydrocarbons (PAHs) are hazardous contaminants found in air, water, soil and sediments. Although PAHs may undergo chemical oxidation, bioaccumulation, photolysis, volatilization and adsorption, microbial degradation is the major process that affecting PAH persistence in nature. The use of microorganisms for bioremediation of PAH-contaminated areas seems to be a promising technology for recovery of polluted sites. Biodegradation of PAHs depends on the environmental conditions, chemical structure and nature of the chemical compounds, soil properties, number and type of the microorganisms. Low-molecular-weight PAHs (two or three rings) are relatively volatile, soluble and more easily degradable. Higher-molecular-weight compounds (four or more rings), which are strongly sorbed to the organic matter are relatively unavailable for degradation processes. During the past years, a variety of microorganisms have been isolated and characterized for the ability to degrade different PAHs via either metabolism or cometabolism. In the presence of oxygen, PAH compounds represent a significant source of energy and carbon for bacteria.

In this work the biodegradation of the contaminants of real soil samples by indigenous microorganisms was studied under aerobic conditions at room temperature using laboratory glass columns. Two soil samples were collected from the storage area of wooden railway sleepers impregnated by oil preservatives.

Bacterial degradation activity was monitored by respirometry via the rate of O\textsubscript{2} consumption and CO\textsubscript{2} production, respectively. The biodegradation experiments have been carried out in the laboratory columns for 20 and 50 days, respectively, with no inoculation of bacteria, only with the use of the original bacterial strains. Soil samples were humidified with water and an inorganic nutrient solution to increase the degradation rate. The results showed that the use of indigenous microorganisms could be considered as a potential tool for the biodegradation. The biological degradation of PAHs is a suitable alternative technique to the technologies using physical and chemical processes in terms of the ecologic and economic aspects. Based on the results of degradation test it is possible to evaluate certain trends and determine the theoretical maximum rate of biodegradation of the specific contaminants close to ideal conditions. The biodegradation of contaminants at the site can be improved in combination with other remediation methods (e.g. bioventing).

Acknowledgement: This work has been supported by the Marie Curie Programme FP7-People-2013-IAAP-WaSClean project No 612250, Slovak R&D Agency project No APVV-10-0252-WATRIP, NATO SPS Multi-Year Project EAP.SFPP 984403 and VEGA-2/0158/15. Moreover, the support of the Operational Programme Research and Development through the project: Centre of Excellence for Integrated Research of the Earth’s Geosphere (ITMS: 26220120064), which is co-financed through the European Regional Development Fund is greatly acknowledged as well.
Exploring polymer inclusion membranes as a basis for a new sensor in metal speciation studies

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Polymer inclusion membranes (PIMs) are a kind of functionalized membranes presently used for different separation purposes, mainly metal preconcentration, removal of pollutants, and elimination of interferences [1]. In this work we will use the PIM for metal speciation purposes.

A PIM consists of a carrier entrapped in a polymer matrix, which confers the mechanical strength to the membrane. In some cases a plasticizer is included in the formulation to provide the necessary elasticity. The carrier is the active component responsible for the transport of the target analyte from the donor solution to the acceptor solution (facilitated transport).

We have investigated the usefulness of PIMs in metal speciation studies and for metal bioavailability sensing. We have chosen Zn as a case study and the composition of the donor phase was fixed at half-strength Hoagland solution. The PIM designed for Zn transport consists of PVC as a polymer and di-(2-ethylhexyl) phosphoric acid (D2EHPA) as carrier. The membrane is placed in a glass device [2] with 0.01M nitric acid as acceptor solution.

The flux of zinc through the membrane was measured for a time period of 24 hours for different total metal concentrations (15µM, 35µM, 50µM and 70µM), and we could observe a linear relation between both variables. We also tested the influence of the presence of different organic ligands by adding to the donor solutions ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citrate, histidine, and humic acid. Finally, experiments in 0.01M potassium nitrate solution were performed with four different zinc concentrations in order to obtain data on Zn flux in a simpler system facilitating the modelling of the PIM-based sensor system.

References:

Acknowledgement: The financial support of the Spanish Government through research project CTM2013-48967 is acknowledged.
Removal of Methylene Blue and Trimethoprim from Aqueous Solutions using Doped Ti-Pillared Clays

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The use of sunlight as a source of energy for the removal of pollutants in wastewater arouses great interest. Emerging contaminants (pharmaceuticals, steroids and hormones, personal care products, antiseptics, surfactants…) have to be removed in wastewater treatment plant effluents [1]. New efficient materials based in titanium-pillared montmorillonite are here studied, efficient as photocatalysts and adsorbents of pollutants.

A titanium polycation solution, [(TiO)₂₈(OH)₁₂]⁴⁺ [2], was prepared by slow addition, under vigorous stirring, of TiCl₄ to absolute ethanol, until a homogeneous yellowish solution was obtained. This solution was added to a previously prepared solution of glycerine in distilled water. The new mixture was maintained under stirring for 3 hours [3], and then was dropwise added to a previously prepared montmorillonite (M) aqueous suspension, with a Ti/clay ratio of 40 mmol/g, aging the new suspension under magnetic stirring for 18 h. Then, the solid was separated by centrifugation, washed by dialysis for 2 days, dried overnight at 70°C and finally calcined at 500°C for 2 h at a heating of 1°C/min. For the doped solids, an appropriate amount of the dopant cations was added to the TiCl₄ solution, using a doping cation/Ti⁴⁺ ratio of 10:90.

The incorporation of the dopant cations induced important changes in the properties of the final solids (which can be seen as nanocomposites composed of one part of TiO₂, three parts of clay and the doping elements) with large basal spacing, specific surface area, porosity and acidity.

Photocatalysts have been evaluated in the degradation of methylene blue in water by sunlight or in the dark. The incorporation of Ti polycations doped with different elements improved the photoefficiency of the catalysts, reaching slightly higher conversions in experiments both with or without light. Concerning recycling of the catalysts, doping with Fe³⁺ or Cr³⁺ led to the best results, as concluded from the degradation levels obtained in the second cycle, even in the absence of light. The results are not conclusive, as the clays strongly adsorbed the dye.

MTi-Fe and MTi-Cr photocatalysts have also been evaluated in the adsorption of trimethoprim (TMP), a bacteriostatic antibiotic derived from trimethoxybenzylpyrimidine, obtaining removal percentages close to 75% after 5 or 10 minutes of adsorption using 254 nm UV light, compared to the 150 minutes needed to reach the same adsorption percentage using the bare clay. Degradation of TMP was also accomplished using natural light; degradation was observed after 15 minutes using the clays containing Ti, Ti/Fe or Ti/Fe, although the byproducts of degradation could not be quantified. The pillared clays maintained the same degradation effectivity using natural light, confirming their high activity, while the parent montmorillonite showed decolorization, but not degradation, as no change in the positions of the UV-Vis bands observed, but only a reduction of the intensities of TMP bands. So, the removal is mainly due to adsorption, probably via hydrogen bonds between NH₂ groups in TMP and siloxane or silanol groups from montmorillonite. Pillared clays showed clear changes on UV-Vis bands, confirming the oxidation of TMP.

References

Acknowledgement - MINECO (MAT2013-47811-C2-R) and FEDER, FAPESP, CAPES (DGPU 317/2015) and MECD (PHBP14/00003); CNPq, Contrato predoctoral de la Universidad de Salamanca (BG).
Adsorption of glyphosate in sepiolite grafted with chloropropyltriethoxysilane (CIPTES)

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The accelerated development of agriculture in the last decades has increased the need to use herbicides. The herbicide Glyphosate (2-[(phosphonomethyl)amino]acetic acid) is a non-selective, post emergent and broad-spectrum herbicide with widely known applications in agriculture [1]. There is currently concern on glyphosate leaching from the root zone into drainage water and groundwater, and it is classified as toxic to aquatic life with long lasting effects [2]. The aim of this work is to investigate the removal of glyphosate from aqueous solution using sepiolite grafted with the alkoxide chloropropyltriethoxysilane (CIPTES). Natural sepiolite from Vallecas (Spain) was purified by sedimentation. The adsorbent was prepared stirring 10 g of purified sepiolite and 50 cm³ of CIPTES (at a 1:5 molar ratio), for 48 hours under inert atmosphere. The solid was washed several times with toluene, ethanol and water and overnight dried in an oven at 70ºC and the material thus obtained was designated as Sep-CIPTES. The adsorption experiments using typical bath procedures involved the study of two key parameters: kinetics (varying the time of contact between adsorbent and glyphosate) and equilibrium experiments (varying the concentration of glyphosate in solution). The amount of adsorbed pesticide in each unit time per unit mass of adsorbent was calculated by the equation: \[ q_t = \frac{(C_i - C_f) V}{m} \]. For the kinetics study 0.05 g of functionalized clay were placed in glass vials with 5 mL of a solution of glyphosate (glyphosate + Milli-Q water and/or complex solution) at a concentration of 300 mg·dm⁻³ Different times (between 1 and 1440 min) were used and centrifugation for 20 minutes at 3000 rpm. The equilibrium adsorption experiments were carried out under the same conditions of the kinetics studies, fixing the optimum time (24 hours) and varying the glyphosate concentration (1-500 mg·dm⁻³). From the X-ray diffractogram of sepiolite clay, it is observed that the purification process was effective, finding only the characteristic peaks of sepiolite. By infrared spectroscopy it was possible to observe changes in the region between 1439-1277 cm⁻¹ for the functionalized material, probably because of the bonds between silanol groups of CIPTES and sepiolite –OH groups.

![Figure 1: a) Kinetics curve of glyphosate adsorption onto Sep-CIPTES, and b) glyphosate adsorption isotherm for Sep-CIPTES.](image)

The kinetic studies reveal that adsorption fits best to a pseudo-second order model, concluding that the adsorption process depends on the interactions between the adsorbent and the adsorbate. The equilibrium study set in the models of Freundlich (\( k_F = 0.67 \)) and Langmuir (\( q_m = 10.73 \)). The isotherm obtained was classified as L-3 type, according to the Giles classification [4]. The adsorbent Sep-CIPTES showed an adsorption capacity (\( q_e \)) of about 30 mg/g.

References

Acknowledgement - The authors thank MINECO and FEDER (MAT2013-47811-C2-R), FAPESP, CAPES (DGPU 317/2015) and MECD (PHBP14/00003); CNPq.
White and Red Brazilian São Simão’s Kaolinite–TiO₂ Nanocomposites as Photocatalysts for Toluene Degradation from Aqueous Solutions.

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One of the greatest current concerns of humankind is to control and prevent environmental contamination; advanced techniques that can diminish or remove pollution, among them photodegradation, are mandatory. The presence of volatile organic compounds (VOCs) in ground water is a major concern to all who use ground water as a drinking water source because many of these compounds can adversely affect human health. In this sense the advanced oxidation processes (AOPs) can induce the oxidation of various complex organic compounds such as pesticides, herbicides, drugs and dyes, turning them into products more easily degradable by biological methods. The biological processes associated to AOPs can thus become efficient for wastewater treatments. The advantage of these processes is that there is a true destruction of the pollutants and not a transfer of them from one phase to another, as it occurs in other treatments such as adsorption processes. For the various AOPs, heterogeneous photocatalysis stands out, involving the use of UV radiation that induces the surface of the semiconductor such as titanium oxide, zinc oxide, etc., to generate hydroxyl radicals able to oxidize various organic compounds [1-3].

This work reports the synthesis and characterization of white and red kaolinite-TiO₂ nanocomposites synthesized via sol-gel method, and their use as catalysts in the photochemical degradation of toluene, a significant VOC. White and red kaolinite-TiO₂ nanocomposites were prepared by a sol-gel method, using titanium bis(triethanolamine) diisopropoxide as a precursor. Thermal treatment of the composite initially formed gave rise to various composites, in which the clay changed from kaolinite to metakaolinite at 700°C, and titanium species were initially incorporated forming an amorphous phase, coordinated to hydroxyl, isopropoxide and triethanolamine groups at 100°C, being transformed to anatase at 400°C, to Al₄Ti₂SiO₁₂ at 700°C, and again forming anatase at 1000°C. This structural evolution strongly affected the photodegradation catalytic behavior; the solid calcined at 400°C, formed by red and white kaolinite and anatase, showed the best behavior.

Almost total degradation of toluene was observed for reaction times of ca. 60 min. All the solids efficiently degraded toluene; the best results were found for the solid heated at 400°C, which degraded 90%. On extending the photochemical treatment up to 2880 min, higher mineralization levels were reached. The synergic influence was confirmed comparing to the results from isolated components (titanium oxide and kaolinite), observing that the formed titanium-kaolinite nanocomposite display a fundamental key in the photodegradation pathways. Kaolinite promotes the dispersion of TiO₂ around the clay surface and into the interlayer spaces and promotes the fast degradation of toluene; kaolinite promotes the interaction with toluene and the titanium dioxide dispersed in the matrix promotes the generation of OH* radicals.

References

Acknowledgement - The authors thank MINECO and FEDER (MAT2013-47811-C2-R), FAPESP, CAPES (DGPU 317/2015) and MECD (PHBP14/00003), CNPq, Contrato predoctoral USAL (BG).
Undergraduate Research and Training in Ion-Beam Analysis of Environmental Materials

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We have an active undergraduate research program at the Union College Ion-Beam Analysis Laboratory (UCIBAL) focused on the study of pollution in Upstate New York. Accelerator-based ion-beam analysis (IBA) is a powerful tool for the study of environmental pollution because it can provide information on a broad range of elements with high sensitivity and low detection limits, is non-destructive, and requires little or no sample preparation [1]. It also provides excellent training for the next generation of environmental scientists. Beams of protons and alpha particles with energies of a few MeV from the 1.1-MV tandem Pelletron accelerator (NEC Model 3SDH) in UCIBAL are used to characterize environmental samples using IBA techniques such as proton-induced X-ray emission (PIXE), Rutherford back-scattering (RBS), and proton-induced gamma-ray emission (PIGE). Recent projects include the characterization of atmospheric aerosols in the Adirondack Mountains [2], the study of heavy metal pollutants in soil and lake sediments, the investigation of possible mercury emissions from crematoria [3], and the search for heavy metals in artificial turf in-fill [4]. We will describe our research program and discuss a few of the recent projects in detail.

References

Acknowledgements - The authors thank the NY NASA Space Grant program, the Union College Research Fellowship Program, and the Union College Department of Physics and Astronomy for research support.
Adsorption of Se(IV) and Se(VI) on UiO-66-based metal-organic frameworks: comparing experiments and theoretical calculation

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Metal–organic frameworks (MOFs) are a class of porous crystalline materials consist of metal-oxide units combined with organic linkers [1]. They have been widely used in gas storage [2] and adsorption [3], metal and organic pollutants adsorption from aqueous solution [4]. UiO-66, a MOFs material consists of hexa-nuclear zirconium groups linked with terephthalates [5], was firstly synthesised by Cavka et al. in 2008 [6]. Because the Zr-carboxylate bond is strong, UiO-66 shows better physical and chemical stability than other MOFs materials [7].

In the present study, two types of UiO-66 with different shapes (cubic and sphere) and their corresponding of NH₂ functionalized UiO-66 (UiO-66-NH₂) were synthesized using hydrothermal and microwave methods, respectively. The prepared materials were characterized using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The adsorption behaviors of Se(IV) and Se(VI) and the factors influencing the adsorption were investigated using batch experiments. The adsorption mechanisms were revealed based on the FTIR and zeta potential analysis. Moreover, the adsorption process were simulated using density functional theory (DFT) calculations.

The results showed that all four types of MOFs had similar crystalline structure, with particle sizes of 100-200 nm. The UiO-66-NH₂ synthesised by microwave method have largest surface area. The adsorption of Se(IV) was higher than Se(VI), and UiO-66-NH₂ had greater adsorption capacity than UiO-66, which suggests different interaction mechanisms of Se(IV) and Se(VI) with MOFs. The MOFs synthesised using microwave method have better adsorption capacities to Se(IV) and Se(VI) than those paredpared using hydrothermal method. The results indicate that not only the BET surface area but also the surface properties could affect the adsorption of Se(IV) and Se(VI). The DFT results showed that the binding energy of Se(IV)/(VI) with UiO-66-NH₂ are much higher than Se(IV)/(VI) with UiO-66, which is in agreement with the batch experimental results. The major adsorption mechanisms are interactions of –OH and –NH₂ groups with Se(IV) and Se(VI). The present study showed that UiO-66 and UiO-66-NH₂ could be promising adsobents for Se(IV) and Se(VI) removal from water.

References

Acknowledgement – This research was funded by the National Natural Science Foundation of China (Grant No. 51379009)
CO$_2$ capture over modified zeolite Y

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Carbon dioxide is the major greenhouse gas that contributes to global warming. Adsorption with solid sorbents is one of the most promising option to reduce of CO$_2$ emission. Zeolites are microporous crystalline materials comprised of aluminum and silicon oxides. Due to high adsorption affinities and high selectivity, aluminosilicate are a suitable material for CO$_2$ capture.

In this study zeolite Y was modified with alkali and alkaline earth metal solutions in order to improve their adsorption capacities. Cation exchange of the sodium forms of zeolite Y was performed using 1.0 molar chloride solutions of suitable cation (lithium, potassium, magnesium, calcium and ammonium). The exchange samples were washed with distilled water and heated at 473 K. The ammonium form of zeolite Y was calcined at 673 K to obtain hydrogen form of zeolite Y.

The samples were characterized by XRD, SEM-EDX, and nitrogen adsorption-desorption at 77 K. The CO$_2$ uptake was determined by BET isotherm measurement carried out at 298 K and pressure up to 0.95 atm.

The experimental results show that both the type and the amount of ion exchange of cations have a significant influence on the adsorption of CO$_2$. The largest CO$_2$ capacities were obtained for materials containing the alkali metals $Li \sim Na < K$. The presence of the alkaline earth metal led to a decrease in the adsorption capacity of carbon dioxide.

Acknowledgements
Andżelika Gęsikiewicz-Puchalska thanks for support from the Polish-Norwegian Research Programme operated by the National Centre for Research and Development under the Norwegian Financial Mechanism 2009-2014 in the frame of Project Contract No Pol-Nor/237761/98.
Kinetics of Adsorption of Polyethylene Oxide (PEO) onto a Colloidal Latex Particle

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Water soluble polymers are widely used as flocculants in various industrial fields to control the stability of colloidal dispersions. They adsorb onto particle surface and induce flocculation. Several elementary processes occur simultaneously among which adsorption kinetics of polymers onto colloidal particles is a key process. However, the mechanism of adsorption process in relation to flocculation dynamics is not completely understood yet. To clarify the kinetics of adsorption, we applied neutral polymer, polyethylene oxide (PEO) with different molecular weight to observe how particle charge is shielded by adsorbed polymer chains. Experiments were carried out by detecting electrophoretic mobility (EPM) and hydrodynamic layer thickness of adsorbed polymer as functions of polymer dosage and ionic strength.

Table 1: Corresponding molecular weight of different types of well-defined PEO

<table>
<thead>
<tr>
<th>Well-defined Polyethylene Oxide (PEO)</th>
<th>Commercial PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample name</td>
<td>SE-150 SE-70 SE-8 SE-2</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>8.85x10⁵ 5.1x10⁵ 9.5x10⁴ 2.6x10⁴ 5x10⁶</td>
</tr>
<tr>
<td>Mw/Mn</td>
<td>1.08 1.05 1.04 1.20</td>
</tr>
</tbody>
</table>

Monodisperse negatively charged polystyrene latex (PSL) was prepared by the standard emulsion polymerization of styrene in the absence of surfactant. The diameter of particle was determined by electron microscopy as 1.36±0.01μm. Well-defined polyethylene oxide (PEO) produced from TOSOH CO.(Japan) and commercial PEO from Aldrich Co. Ltd were used. Their molecular weight and index for monodispersity are given in Table 1. Ionic strength was controlled by potassium chloride (KCl) solution.

Result in Figure 1 indicated the relationship between electrophoretic mobility (EPM) and polymer dosage. It is demonstrated that in each ionic strength, absolute value of mobility decreased remarkably with addition of polymer at low concentration but slowly reached a plateau with increase of polymer concentration. This result showed that neutral polymer would decrease the absolute value of electrophoretic mobility (EPM) of colloidal particle. Additionally, higher the ionic strength, larger the molecular weight of polymer, the shielding effect of polymer chains was found to be more pronounced. Figure 2 indicated the hydrodynamic layer thickness of crude PEO as a function of polymer dosage at ionic strength.

References
Transport, retention and sorption interaction of functionalized multi-walled carbon nanotubes in goethite-coated quartz sand

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ABSTRACT

Batch and water-saturated column experiments were conducted at low concentrations (1mg L⁻¹) of functionalized ¹⁴C-labeled multi-walled carbon nanotubes (MWCNTs) in a heterogeneous porous medium composed of quartz sand (QS) and goethite-coated quartz sand (GQS) mixed with different mass ratios and different grain sizes (240, 350 and 607µm). A numerical model that accounted for both irreversible time- and depth-dependent blocking functions was used to fit both breakthrough curves (BTCs) and retention profiles (PRs) of MWCNTs. Results from both the batch and water-saturated column indicated that the sorption, transport and retention of MWCNTs were sensitive to the goethite coating and sand grain size. Higher mixing mass ratios of GQS and lower grain sizes increased the sorption and the retention of MWCNT in this porous medium.
Efficient electro-Fenton for organic pollutants removal: cathode interface modification to improve performance

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In recent years, the abatement of biorefractory and toxic pollutants has received global ever-increasing interests. The applications of electrochemistry for environmental pollution abatement have been thoroughly investigated, possessing the advantages of environmental compatibility, versatility, high energy efficiency, and amenability of automation and safety. Especially, electro-Fenton process has attracted considerable attention, generating hydrogen peroxide in situ via a two-electron reduction of O₂ on suitable cathode (Eq.(1)) [1-3].

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \] (1)

Great efforts have been paid to sound electrode materials exploration, efficient processes and novel reactor development, as well as typical organic pollutants degradation mechanism investigation [3-5].

Cathode plays an important role on electro-Fenton performance, and cathode modification and interface regulation seems very necessary and vital. This work summarized our recent works in this area to improve electro-Fenton treatment efficiency in view of application, including cathode modification by chemical or electrochemical method to enhance hydrogen peroxide production, heterogeneous catalyst fabrication and their degradation mechanism, and novel cathode system development. These cathode materials and system would greatly enriched electro-Fenton process and extended its application for environmental remediation.

References

Acknowledgement - The authors thank supports from Natural Science Foundation of China (no. 21273120 and 51178225), National High Technology Research and Development Program of China (2013AA065901 and 2013AA06A205).
Environmental impact of Bouhaloufa dam construction in El Tarf (North Eastern Algeria)

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The present work is the impact synthesis report on the environment prior to the construction of Bouhaloufa dam located 30 km south of the wilaya of El Tarf, on the Layouts its irrigation system and perimeters transfer of river inter-basin water. With an area of 176.50 km², this area is one of the largest hydraulically with 40% of surface water resources. Low permeable soils explain the presence of many swamps covering much of the plains.

![Figure 1. Location map of the study area](image-url)

The dam’s supply sources are the rivers of Bouhaloufa, Kebir East and Boulabtane with an inter annual contribution of nearly 90.21 Hm³. Some studies reveal the existence of a shallow water table (2m) contained in alluvial terraces captured by wells.

The purpose of the project being the irrigation view agriculture is the fundamental potential of the region; it will induce a positive effect for the region by better use of land and a good agricultural valuation of water resources of the study basin.

The development of this work aimed at the detailed description of the watershed: the geographical and natural characteristics inventory of water sources and industrial and agricultural activities. The diagnosis of water resources was related to the amount of surface water and groundwater quality and the determination of pollutants and their origins appealed to the physicochemical analyzes estimates of the amount of organic matter and microorganisms in the water. Finally the determination of vulnerable areas (impact of the dam on the environment) using a problem-solving approach focused on water treatment for the preservation and regional planning.

Moreover, the threats that weigh on the fragile environment are many; influences on the water conditions, recharge diminution of these systems, alteration of surface water quality, vulnerability of water from the shallow aquifer, threatening the loss of wildlife of the region.

The impact on the environment is not negligible, the intervention must be the strict minimum and not to disturb the balance of nature by pollution, whatever its origin.
Particle Induced X-ray emission (PIXE) method applied to the analysis of environmental samples

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Abstract. In this study we applied PIXE spectrometry with aim to determine the heavy metal content in moss samples collected from different geographical zones in Romania, which can be used as bioindicators. The PIXE experiments were performed using a proton beam provided by the 3 MV Tandetron™ particle accelerator from the National Institute for R&D in Physics and Nuclear Engineering “Horia Hulubei” (IFIN-HH), Magurele-Bucharest. The trace elements in samples, mosses and certified standard, were analyzed. The elements identified were: Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn and As, and quantitatively evaluated were: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu and Zn. The concentrations values of these heavy metals in the analyzed samples by PIXE technique were compared with the results obtained by Atomic Absorption Spectrometry (AAS) method.
Impact of organic compounds on the synthesis of phases and properties of sand-lime products

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Sand-lime products are manufactured using autoclaving process (at the temperature of 200°C and under a high pressure). Sand-lime products can be applied in various environments. However, it is recommended to verify each time the environmental conditions and to properly choose the products designed to be used in a given environment due to the modifications of sand-lime mass that has been carried.

The study began with an analysis aimed at improving, modifying and reducing the consumption of raw materials or energy used for the production of sand-lime products. The priority properties of the resulting products have been established for a specific modification. These were properties important to consumers, such as strength or water absorption. Disposal of waste and the possibility of using organic components has become a significant problem.

Therefore, an analysis of the possibility of using waste or organic materials in the sand-lime mass has been carried out. Substances were selected by analyzing their compositions, i.e. These are components rich in elements and chemical compounds (such as aluminum and phosphorous) as well as in microorganisms. Numerous innovations indicate the right direction of the action. Watabe A. and others (patent 62-090530) propose introducing to the humus an weight increasing activator, which allows the formations of porous limestone.

Introducing of organic compounds, humus or biohumus in the production stage is chemically neutral for sand-lime products, because the process of the withering away of any micro-organisms and possible bacterial cultures already occurs at 134°C, and the production of silicates requires a temperature of 200°C.

The study involved 4 types of humus and biohumus. The tests were made using microscopes: KOZO OPTICS XJS 800 FL and LSM 700 by ZEISS, based on which the composition of examined substrates was identified. The studies have shown the presence of plant debris and in biohumus also microorganisms. On the basis of the analysis the composition of modified mixture was developed. The modifier appeared in a liquid form in order to streamline the modification process (an admixture can be easily combined with water while stirring of the sand-lime mass).

In order to select the modifier for silicate mass a multicriteria technical and economic analysis (methods of multivariate analysis) has been carried out. Graphic interpretation makes it possible to determine the correlation between simultaneously compared additives and their criteria. It is presented in biplot. Numerous statistical methods contained in STATISTICA 10.0 are used for the graphic presentation of analyzed correlations. For this purpose, most commonly used are located in the module “Multivariate Exploratory Techniques” methods of factor analysis and principal components, correspondence analysis and multidimensional scaling. Each of them allows the graphic presentation of the results and shows the greatest possible amount of information from the analyzed data.

The active variables for the analysis are variables that affect the microstructural properties of sand-lime products, economy and ecology. The passive (additional) variables are those which in a given case affect only the aesthetics of silicates and photosynthesis (characteristic only for plants). Biplot is created on the basis of the covariance matrix in order to obtain information about the diversity of individual variables.

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Table 1: The matrix of experiment planning and the levels of independent factors
Removal of humic acid from aqueous solution by kaolin from Ivory Coast

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Humic acid (HA) is a natural macromolecular and dissolved organic matter formed by decomposition of natural organic matter, which is ubiquitous in surface water and ground water. Its presence in the water supply leads to flavor, color and an unpleasant odor. In addition, HA is recognized as key precursor of carcinogenic by-products during the step of disinfecting the water (chlorinated treatment) [1]. Therefore, many efforts were made to minimize and remove HA in drinking source water.

The purpose of this work is the development of a local biomass material, namely raw kaolin, into adsorptive material to remove HA from aqueous solutions. The raw clay and its purified fraction (diameter inferior to 2 µm) were characterized by elemental analysis, X-ray diffraction (figure 1), N₂ adsorption and pH_{ZPC} measurements.

Different experiments were conducted using a batch process, to study the effect of contact time, initial HA concentration, pH, clay dose and temperature. The adsorption equilibrium time was dependent to initial HA concentration. The kinetic data was analyzed using pseudo-first order and pseudo-second order kinetic models and the data fitted well to the pseudo-second-order adsorption model. Adsorption was heavily pH-dependent, with lower uptake at higher pH values due to increased ionization of the humic substances. Higher HA adsorption was found at low pH indicating that electrostatic interaction played an important role between HA and kaolin. The isotherm adsorption data was analyzed using Langmuir isotherm model and it was found that this model well fitted. The maximum adsorption capacity corresponding to monolayer coverage at 20 °C was about 11 and 115 mg/g at pH = 7 and 3 respectively according to the Langmuir model. The value at pH = 3 is approximate to that reported for Aminopropyl functionalized SBA-15 at pH=3 (117 mg HA/g) [2], while it is higher than that reported for purified bentonite at pH =3 (70 mg HA/g) [3]. Thermodynamic study showed that the adsorption of HA onto purified clay was feasible, spontaneous and endothermic under investigated temperatures 20-35°C. According to the results of this work it may conclude that kaolin from Ivory Coast is a promising adsorbent for removing HA from water.

References
Ion-selective Electrodes (ISEs) for Cd$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$: Requirements for Correct Measurements and Application in Analysis of Potable, Industrial and Waste Waters

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Ion-selective electrodes are widely used for non-destructive, rapid, sensitive and precise determination of many ions in a great variety of media and therefore provide a powerful analytic tool. If ISEs produced by Orion Research are universally recognized, other manufactured electrodes are cheaper and easy to supply; some electrodes can be prepared in the laboratory. These electrodes must be tested under well-defined criteria. Results scattering in the scientific study and variability of analytic conditions in each specific case, make it difficult the direct exploitation of the results accumulated by other researchers. So, a systematic survey of some ISEs to be applied later in water pollution checking is suggested. This study accounts for the more or less facility of use, the sensitivity limits, the interferences find and describe the titration procedures developed.
Impedance spectroscopy and conductometric biosensing for probing catalase reaction with cyanide as ligand and inhibitor

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ABSTRACT
In this work, a new biosensor was prepared through immobilization of bovine liver catalase in a photoreticulated poly (vinyl alcohol) membrane at the surface of a conductometric transducer. This biosensor was used to study the kinetics of catalase–H₂O₂ reaction and its inhibition by cyanide. Immobilized catalase exhibited a Michaelis–Menten behaviour at low H₂O₂ concentrations (b100 mM) with apparent constant K_M_app=84±3mM and maximal initial velocity V_M_app=13.4 μSmin⁻¹. Inhibition by cyanide was found to be non-competitive and inhibition binding constant K_i was 13.9±0.3 μM.

The decrease of the biosensor response by increasing cyanide concentration was linear up to 50 μM, with a cyanide detection limit of 6 μM. In parallel, electrochemical characteristics of the catalase/PVA biomembrane and its interaction with cyanide were studied by cyclic voltammetry and impedance spectroscopy.

Addition of the biomembrane onto the gold electrodes induced a significant increase of the interfacial polarization resistance R_P. On the contrary, cyanide binding resulted in a decrease of R_P proportional to KCN concentration in the 4 to 50 μM range. Inhibition coefficient I_50 calculated by this powerful label-free and substrate-free technique(24.3 μM) was in good agreement with that determined from the substrate-dependent conductometric biosensor (24.9 μM).
Hydrodynamics and mass transfer in a stirred tank reactor: Application to the degradation of pharmaceutical pollutants in wastewater

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Aeration of a liquid phase by gas is the basis of many chemical oxidation, absorption and biological treatments of urban wastewater processes. To optimize the performance of oxygen transfer, it is essential to consider the hydrodynamic phase that determines the exchange surface, the thermodynamic properties of phases that control the exchange and the transfer coefficient material between the gas bubbles and the associated liquid.

In this study, the experimental gas (air)-liquid (water) reactor consists essentially of a flat bottom tank (Dₑ = 23.6 cm) designed according to the standard configuration of HOLLAND with four radial baffles, placed on the wall of the tank to avoid the formation of vortex, and a stirrer. The gas, supplied by a blower, is injected in the reactor via a single nozzle sparger (dₙ = 6 mm). Six configurations for the stirrer have been tested for the hydrodynamic study: a simple configuration called single-stage (Rushton turbine and turbine with six inclined blades) and a two-stage configuration (combination of two Rushton turbines, combination of two turbines with six inclined blades, combination of a Rushton turbine above and a six inclined blades below and finally a combination of a six inclined blades above and a Rushton turbine below).

For these configurations, the gas hold-up was measured at room temperature and atmospheric pressure while two process parameters varied: the superficial gas velocity (from 0 to 2.8x10⁻³ m.s⁻¹) and the stirrer rotational speed (from 0 to 450 rpm).

The three hydrodynamic regimes (short circuit, mixing and flooding) were observed for both the single-stage configuration and the two-stage one. The results show that the gas hold-up gets a maximum value for the mixed two-stage combination (six inclined blades turbine above and Rushton turbine below). This optimal combination was retained for hydrodynamics and mass transfer study under various conditions of superficial gas velocity (from 0 to 2.8x10⁻³ m.s⁻¹) and stirrer rotational speed (from 0 to 450 rpm). The residence time distribution (RTD) was conducted using the well-known tracer method. The experiments show that the stirred reactor is perfectly mixed. The photographic method was employed for the bubble size distribution and the gasing out method was applied for the determination of the volumetric mass transfer coefficient. The influence of the superficial gas velocity and stirrer rotational speed on oxygen mass transfer was related to gas hold-up and bubble size. Oxygen transfer increases with increasing gas hold-up and decreasing with bubble size. Wastewater treatment experiments were then carried out in order to evaluate the removal of pharmaceutical pollutants (antibiotics) by the lab scale reactor. The first results are very interesting and the reactor designed seems to be a promising process for the degradation of pharmaceutical pollutants present in wastewaters.
Wastewater treatment: adsorption of antibiotics on activated wood biochar with carbon dioxide

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Conventional wastewater treatment processes are designed to achieve improvements in the quality of the wastewater. The treatment consists of a combination of physical, chemical, and biological processes. These various processes may reduce: suspended solids, biodegradable organics, pathogenic bacteria and nutrients including nitrates and phosphates. However, pharmaceuticals have been detected in effluent waters of wastewater treatment plants worldwide. This is because of their increased use as well as that wastewater plants are not specifically designed for pharmaceuticals removal. This issue should be of concern because these trace amounts might cause potentially harmful changes in aquatic life and negative effects on humans [1]. Therefore, new developments in the water treatment field especially for better pharmaceuticals removal efficiencies are required. The objective of this study is to develop a sustainable and a cost effective water treatment process based on the adsorption of pharmaceutical pollutants. For this purpose, an experimental methodology was set up using a natural adsorbent. This study highlights the preparation of wood char by pyrolysis, its activation with carbon dioxide and its characterisation. In the present paper, the removal of an antibiotic residue (spyramycin) from water by adsorption on activated wood char was studied. The adsorption experiments were performed in static mode and the influence of several parameters such as: the contact time, the antibiotic initial concentration, the activated biochar mass on the adsorption phenomenon and the removal efficiency was studied.

These experiments showed that the adsorption depends on the particle size of wood char. In fact, the amounts of antibiotic (spyramycin) adsorbed by the fine particles (dp≤500 μm) are relatively higher compared to those of coarser particles. For a solid/liquid ratio (char/water) of 0.5g/L, the removal efficiencies reach a value of 66% for an antibiotic initial concentration of 10 ppm. This efficiency could be easily improved by increasing the adsorbent (biochar) mass. The experimental results also showed that the adsorption kinetics of spyramycin by the wood char fits well with the pseudo-first order model [2] and exhibits three-stage intra-particle diffusion mode. The adsorption capacity of the wood biochar increases with the antibiotic initial concentration in water and the relative experimental adsorption isotherm (type I) is well described by the Freundlich isotherm model [3].

The overall results of this study show that wood biochar activated with carbon dioxide could be considered as a very effective and promising material for antibiotics removal from wastewater.

References

Effect of salt concentration in flow-electrode on flow-electrode capacitive deionization

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Flow-electrode capacitive deionization (FCDI) have recently been studied due to continuous deionization and a high desalting efficiency originated from the flow-electrode. A flow-electrode with high capacitance and low resistance is developed to operate a highly efficient FCDI system. Therefore, researches on porous materials, conductive additives, and electrolytes constituting the flow-electrode should be conducted for high performance flow-electrode. Therefore, the desalting performances of flow-electrodes with aqueous electrolytes containing various concentrations of NaCl were evaluated to verify the effect of salt concentration in a flow-electrode on desalting efficiency of FCDI. We confirmed the necessity of a moderate amount of salt in the flow-electrode for compensating for the performance reduction of the flow-electrode originated from the resistance of deionized water used as the electrolyte (Figure 1).

![Figure 1: Correlation between desalting efficiency and NaCl concentration in the flow-electrode](image)

References
Sand-lime products in the light of sustainable development

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Human most of his life spent indoors, in buildings - in the microenvironment, which is largely influenced by the properties of the materials of construction. Researchers are looking for modern materials and modify already known, to get friendly to both: humans and the environment building blocks.

Particularly noteworthy are silicate products. These organic products do not emit any harmful substances, and in terms of natural radioactivity are classified as safest materials. During production, there are no additives or chemicals harmful to the environment. The material after demolition can be minced and reused for the production of, and placed in the ground as the rubble does not cause the contamination. Consequently, the sand-lime products are gaining in popularity, they are subjected to numerous modifications designed to improve the material.

The aim of the paper is to present the results of studies of the sand-lime product modified with the addition of polyethylene glycol. The resulting product is characterized by improvement of basic physical and mechanical properties with compare to the traditional products, ecology and biodegradability. Silicate product with the addition of polyethylene glycol can be used as a substitute for defaulting materials in landfills and those that harm the environment.

To obtain the expected physical and mechanical properties of modified silicate, it is important to know the relationship between the microstructure of the material, types of bonds that occur between individual components and the strength of test samples. Microstructure of traditional and modified sand-lime materials, was made using a scanning electron microscope Quanta 250 FEG. The obtained images and EDS analysis identifies a range of reactions and changes in the microstructure, which occurred after subjecting the sample to hydrothermal treatment in an autoclave. In addition, analysis of the mineralogical composition (XRD), allowed for qualitative and quantitative identification of crystalline phases that occur in the material. The phase composition of the test samples was obtained using X-ray diffractometer PANalytical Empyrean. The share of individual phases was determined by Rietveld.
Removal and recovery of cationic dyes from textile wastewater by capacitive deionisation: Synergetic effect mobility – adsorption

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ABSTRACT: The removal and recovery of astrazon yellow 7 GL, a cationic dye, from textile wastewater by capacitive deionisation (CDI) was investigated on a lab. scale CDI module. It was a novel and successful application of CDI. Excellent removal (99%) and recovery efficiencies, limpid treated water and parameters optimization (voltage, flow rate, pH…) were the main findings. It could be a serious alternative to the conventional destructive treatments (adsorption, bacterial, AOP…). The removal efficiency was three times better than the conventional AC adsorption. The research hypothesis was based on the two cationic dye properties: conductance – AC adsorption. Are they synergetic?

INTRODUCTION: The CDI may be considered as a breakthrough in the desalination world. Important research efforts and high investments were accorded to CDI and to electrosorption derived processes [1, 2]. By its simplicity CDI may change the future trends of desalination technologies. Industrial pollution prevention constitutes other potential application area of CDI [3, 4] with unlimited possibilities. This research work presents an original and very important environmental application, rarely investigated by CDI [5, 6], the cationic dyes removal from textile wastewaters. The textile dye conventional treatments (adsorption, bacterial,…) are destructive without water recycling. The modern treatments, AOP and membranes, have serious drawbacks; fouling and cost with membranes and hazardous by products with AOP. The cationic dye conductance and hydrophobicity was the research hypothesis which predicted synergetic effects electrochemical mobility – adsorption on the CDI activated carbon electrode. Confirmation was obtained here with the astrazon yellow 7GL (AY) dye.

RESULTS AND DISCUSSION: The dyes removal efficiency by CDI was three times (Figure 1) higher than the conventional adsorption. The electrochemical desorption and the dyes recovering were almost total (≈99%). More various influencing parameters (applied voltage; pH, flow rate,…) had been systematically studied to optimize the CDI process.

Figure 1: comparison of the electrosorption/adsorption of astrazon yellow dyes on granual activated carbon

References


Physico-chemical characterization of the surface of actinomycetes isolated from soil of Béni amir (Beni Mellal, Morocco) by two methods

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Microbial adhesion to surfaces is the result of physico-chemical interactions between the surface of the microorganism.

Actinomycetes are an important class of microbial resources, they are important producers of antibiotics and other important bioactive substances. Formation of biofilm may promote the production of secondary metabolites.

Physico-chemical properties of actinomycetes surface are evaluated by 2 methods, contact angle measurements (CAM) and Microbial Adhesion to Solvents (MATS). Nine strains, isolated from soil collected from the perimeter of Tadla area Beni Amir Morocco, are grown in the liquid Bennett medium. Measurements of physico-chemical properties were performed in a high ionic strength.

Adhesion of actinomycete strains to different solvents (MATS) shows a greater affinity with chloroform (electron acceptor acid) than hexadecane; this indicates that 62.5% of total cells actinomycetes have an electron donor character (basic). Remaining cells (37.5%) have a low affinity for chloroform reflecting an electron donor character zero or very low. Furthermore, the affinity to diethylether (electron donor solvent, basic) is lower than that of hexane (non-polar), shows an electron acceptor character too low, even zero in 50% of the total strains of actinomycetes. However, the affinity with nonpolar solvents is low and does not exceed 50%, indicated hydrophilic character strains. Angle contact results shows that all tested strains express a hydrophilic character. These bacteria have a strong electron donor character and a low electron acceptor character.
Kinetic and thermodynamic effects influencing the availability of Mg measured with Diffusive Gradients in Thin Films (DGT) devices at different ionic strengths

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Magnesium has many important roles in soils, sediments, minerals and waters [1] so that its availability is an issue of environmental concern. In the last decade, DGT devices have been recognized as suitable tools to measure in situ the availability of metals cations, anions and some emergent pollutants in soils and waters [2-3]. Data reported indicate that non-linear DGT accumulations of Mg are obtained at high ionic strengths (I) whereas the accumulations increase and become linear with time as the ionic strength decreases. Additionally, by using DGT devices with a stack of two resin discs, it is shown that the percentage of Mg accumulated in the back resin disc (%back) decreases as I decreases.

The interpretation of the ionic strength influence on DGT data is still controversial [4]. Here, the phenomena above commented are explained by i) the dependence of both the association rate constant and the stability constant, K, of the reaction between Mg cations and resin sites on I and ii) an electrostatic partitioning of Mg cations at the resin-gel interface.

A model for the interpretation of the Mg accumulation at different ionic strengths is developed. This model considers the diffusion, migration and reaction of the Mg cations in the gel and resin domains where the fixed charges of the resin and the background salt create a continuous electrostatic potential. Good agreement is also obtained with a simpler model where migration reduces to a Boltzmann factor for the partitioning description.

The model involves only the fitting of kinetic and stability constants at the different I values, as partition factors are measured independently from equilibrium accumulations of Rb cations at the same conditions. It is shown that the fitted kinetic association constants follow the Bjerrum kinetic salt effect.

The main effect responsible of the increase of the Mg accumulation as I decreases is the increase of the stability and association rate constants. The effect of the latter is experimentally supported by the decrease of %back as I decreases, whereas the electrostatic partitioning has a negligible influence on %back. The influence of the electrostatic partitioning on the accumulation is always lower than 17% for a deployment time of 24h.

Finally, for salinities lower than 5 mM, it is shown that the binding of Mg is so fast and strong that the simplest perfect sink DGT expression can be used to predict Mg accumulation.

Similar principles are expected to apply for Ca accumulations. In this way, this work is a step forward towards the understanding of the availability of major cations in natural waters.

References

Acknowledgement - Financial support from FEDER and the Spanish Ministry of Education and Science (Projects CTM2012-39183 and CTM2013-48967) is gratefully acknowledged.
One century of the Langmuir adsorption isotherm

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In the beginning of 1916 Irving Langmuir (1881-1957) developed his famous equations relating the amount of gas adsorbed on a surface to the pressure of the gas [1-6]; such equations are now referred to as Langmuir adsorption isotherms. He arrived at them by equating the rates of adsorption and desorption at equilibrium. For the simplest case, that of a gas adsorbed on a smooth surface, he found that the fraction of the surface covered by the adsorbate (coverage), θ, is related to the pressure of the gas, p, by:

$$\Theta = \frac{Kp}{(1 + Kp)}$$

where K is an equilibrium constant for the adsorption process [7].

Chemical reactions often take place more easily next to surfaces where substances in different phases, such as solids and gases, come in contact with each other. During his studies of incandescent light bulbs with rarefied hydrogen gas, Langmuir discovered that a one-atom-thick layer of hydrogen formed on the inside of the incandescent light bulb. Further studies of oil films and other materials led him in 1917 [3-5] to a theory postulating that surfaces resemble a chessboard on which every square can be occupied by only one atom or molecule [8].

In 1917, Langmuir also developed a surface film balance [3], which had many of the same features as that used by Agnes Pockels in her kitchen (described on a letter in German to Lord Rayleigh in 1891). This balance measures the surface pressure of a film, Γ, which is defined as the force exerted on it divided by the length of the edge along which the force is exerted [7], and can be related to the decrease in surface tension from the pure liquid to the solution containing the monolayer: $\Gamma = \gamma_0 - \gamma$.

Irving Langmuir won the Nobel Prize in Chemistry in 1932, for his discoveries and investigation in surface chemistry [9]. The present communication is a chronological review of his main achievements and a tribute to the key role played by his theories in the history of Physical Chemistry of Interfaces.

References
Dealing with electrostatic interactions in the determination of ion binding properties of polyelectrolytes. Extension of the transfer matrix formalism to the full range of ionic strengths

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The transfer matrix formalism is a powerful technique to solve Ising-type models, that has been successfully applied to the determination of ionization and metal binding properties of linear polyelectrolytes [1-3]. However, the method is only feasible when short-range interactions are present (i.e. at high ionic strengths), since the size of the matrices grows exponentially with the range of the interactions.

Here the formalism is extended to include long-range interactions by introducing a modified free energy, which involves parameters that account for the long-range energy in an effective way. They can be systematically calculated by using the Gibbs-Bogoliubov variational principle [4]. The resulting correction to the cluster parameters represents the average changes in the long-range energy when a new local interaction is created in the polymer.

The methodology is illustrated with the calculation of acid-base titration curves of homogeneous and heterogeneous polyelectrolytes and polyampholytes at low ionic strengths and the results compared to Monte Carlo simulations (following a procedure detailed in previous publications, e.g. [5]).

For the studied models, the correction of the site protonation free energy (first order correction) is enough to obtain an excellent, almost exact, agreement between theory and simulations. Corrections to other binding parameters (higher order corrections), such as the nearest neighbour interaction, are also implemented, although very little improvement is obtained.

References
Calcium phosphate mineralization on RO/NF membrane mimetic surfaces in desalination of wastewater

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Domestic wastewater treated by reverse osmosis (RO) and nanofiltration (NF) membranes has been considered as an important supplementary water source for agricultural and industrial applications. However, water recovery by these membrane processes is greatly affected by the presence of sparingly soluble salts, where precipitation of these salts occurs on the membrane surface leading to severe membrane flux decline. Among the salts, calcium phosphate scaling is often the most unavoidable due to the lack of proper antiscalants [1].

In this study, we investigate calcium phosphate precipitation on RO/NF membrane mimetic surfaces from a model solution simulating secondary wastewater effluent during desalination (termed SSE). RO/NF mimetic surfaces were prepared on gold coated silicon wafer (Figure 1A) according to our previous report [2] and then chemically modified with CMTMAC and taurine, respectively. The physico-chemical properties of the prepared surfaces were characterized using ATR-FTIR, XPS, zeta potential and water contact angle techniques. The addition of quaternary ammonium group has resulted in slightly decrease in negative zeta potential, while the addition of sulfonyl group has resulted in slightly increase in negative zeta potential values, as expected (Figure 1B). Calcium phosphate precipitation was monitored by immersing the mimetic surfaces in SSE solution and by following the frequency changes in quartz crystal microbalance. XRD and ATR-FTIR experiments were used to identify the minerals formed on the RO/NF mimetic surfaces. Mineralization experiments on the prepared surfaces showed different rate of mineralization. The screening of surface mineralization may be used for developing surfaces with anti-scaling properties, which may lead to improvement of the RO desalination of wastewater effluents and hence lower cost of water treatment.

References

Acknowledgement – The authors thank Blaustein Center for Scientific Cooperation (Ben-Gurion University of the Negev) and Germany Israeli Foundation for Scientific Research and Development (GIF Grand No- I-1240-307.8/2014) for the financial support.
Intra-specific variation in tree growth under elevated CO₂ and O₃ – A meta-analysis

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Atmospheric CO₂ concentrations are expected to increase throughout this century, potentially fostering tree growth, but this effect could be counter-balanced by O₃ pollution. A wealth of studies have examined the variation in CO₂ responses across tree species but the extent of intra-specific variation in response to elevated CO₂ (eCO₂) has, so far, been examined in individual studies and syntheses of published work are currently lacking. We conducted a meta-analysis on the effects of eCO₂ alone and with O₃ on tree growth (height, stem biomass and stem volume) and photosynthesis across genotypes to examine if there is genetic variation in growth responses to eCO₂ and understand their dependence on photosynthesis. Most of the published studies so far have been conducted in juveniles and in Populus spp., although the patterns observed were not species-dependent. All but one study reported significant genetic variation in stem biomass, and the magnitude of intra-specific variation in the response to eCO₂ was similar in magnitude to previous analyses on inter-specific variation. Growth at eCO₂ was predictable from growth at ambient CO₂ (R² = 0.60), and relative rankings of genotype performance were preserved across CO₂ levels, indicating no significant interaction between genotypic and environmental effects. The growth response to eCO₂ was not correlated with the response of photosynthesis (P > 0.1) and, while we observed 57.7% average increases in leaf photosynthesis, stem biomass and volume increased by 36 and 38.5%, respectively, and height only increased by 9.5%, suggesting a predominant role for C allocation in ultimately driving the response to eCO₂. Finally, best-performing genotypes under eCO₂ also responded better under eCO₂ & eO₃. Further research needs include widening the study of intra-specific variation beyond the genus Populus and examining the interaction between eCO₂ and other environmental stressors. We conclude that significant potential to foster CO₂-induced productivity gains through tree breeding exists, that these programs could be based upon best-performing genotypes under ambient conditions, and that they would benefit from an increased understanding on the controls of allocation.
A protocol for wide range porosity data image acquisition

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A protocol for obtaining soil digital images with a wide range of pore sizes, intended for fractal studies of the porosity, using a photo-camera and a confocal microscope images is proposed. It is the first time that confocal microscopy is used for this purpose. The use of fluorescent compounds to enhance the contrast between the solid and the pore phase is also tested. Artificial soil ground truth images are created through random Sierpinski carpet fractals,

These artificial soil images were used to make a objective comparison of automatic segmentation algorithms for the obtained images. A statistical classification on the performance of several automatic segmentation algorithms for this type of images is shown.

This protocol yields images with high resolution and a broad range in pore sizes, to be used in the characterization of the architecture of the pore space and the study of the flux and transport processes in soils.
Design of a supported liquid membrane system for the determination of Zn bioavailability in natural waters.

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The impact of trace metals on the aquatic environment and their bioavailability depends on the physicochemical nature of the chemical species, and is often correlated to the concentration of free metal ion.

Zinc, that is an essential micronutrient for plants and animals and that can be toxic at high concentrations, is present in natural aqueous systems in free ion form, but to a large degree is also bound to inorganic and organic ligands. These species differ in mobility and bioavailability to the free Zn ion that is thought to be the form in which Zn is mainly taken up by organisms. The accurate determination of free Zn$^{2+}$ in waters and soil solutions is very difficult due to its low concentrations. To this end, several techniques such as Permeation Liquid Membrane (PLM), Diffusive Gradients in Thin-films (DGT), Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) and the Donnan Membrane Technique (DMT) have been used. The PLM technique has the advantages of relatively short analysis time compared to DMT and DGT, preconcentration of the metal species, and selectivity that can be achieved by selecting the appropriate extractant.

In this study, a three-phase hollow-fibre liquid-phase microextraction (HF-LPME) system has been developed for Zn$^{2+}$ transport. This system is based on the use of 2-ethylhexylphosphonic acid (D2EHPA) as the carrier. The influence of the chemical composition on the efficiency of the membrane system has been investigated. The best extraction conditions (approx. 90%) were achieved using a 10$^{-1}$ M HN$O_3$ solution in the stripping phase and a 0.1 M D2EHPA solution in dodecane in the membrane phase. The HF-LPME system was also evaluated in the presence in the feed solutions of different organic ligands, such as Citric acid and EDTA, which form negatively charged complexes with Zn$^{2+}$. Finally, the selectivity of the chemical system with respect to Zn$^{2+}$ was studied in the presence of other divalent ions, such as Cu$^{2+}$, using 0.5 mg·L$^{-1}$ of both metals.

The device was applied to evaluate the free labile fraction of Zn in river water samples, the presence of humic acids, chlorides and sulfates that can form zinc complexes, as well as other metals such as Fe$^{3+}$, results in a decrease in the Zn$^{2+}$ transport. More studies should be done to assess and validate the applicability of this device in determining the bioavailable Zn fraction in natural waters.

Acknowledgment. *The study was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) through the National Programme for Fostering Excellence in Scientific and Technical Research. Project CTM2013-48967-C2-2-P*
Interfaces Against Pollution
Environmental Challenges & Opportunities

Index of authors

Abril, Gwenael: 34
Achterberg, Eric P.: 96
Adachi, Yasuhisa: 51, 73, 229
Agathokleous, Eugenios: 161
Aguerre-Chariol, Olivier: 26
Ahmad, Farrukh: 146
Ahuali, S.: 90, 110
Aidarova, S.B.: 112, 113
Aït-Amar, Hamid: 121
Akkar, M.: 163
Al-Abadleh, Hind A.: 102
Alam, M.: 115, 116
Alberti, G.: 199
Allen, Nick: 102
Altier, Alexandra: 158, 244
Alvarez, Pedro J.J.: 46
Álvarez-Rodríguez, Esperanza: 165
Amrane, Abdeltif: 121
Anderson, Amandine: 31
Anderson, Marc A.: 53, 108
Angulo, Andrea: 49
Antelo, Juan: 98, 189
Anticó, Enriqueta: 81, 124, 222
Antosik, A.K.: 209
Arce, Florencio: 189
Arey, J.S.: 216
Armanious, Antonius: 105
Atteia, Olivier: 68
Auffan, Mélanie: 26
Avena, Marcelo: 65, 167
Avendaño, Lizeth: 96
Avneri, Shani: 63
Baccouche, M.: 131
Badra, Attoui: 232
Bak, Sol-A: 117
Banerjee, Dipanjan: 97
Barba, Ian: 118
Barbier, Karima: 127
Barbosa, Francisco A. R.: 60
Barillon, Rémi: 64
Barroso, Cervera, Angel: 194
Barral, M.T.: 174, 175
Barrientos, Marco: 169, 173
Barrio, Sofia: 117
Bardos, Marta: 119
Bera, O.: 180
Bergel, Alain: 86
Bertois, Henri: 68
Bertrand, Carlos: 217
Bestani, Benoautda: 128
Bi, Guoessé Henri Briton: 142
Bianco, Carlo: 54
Biesheuvel, P.M.: 107, 109, 138
Biñavar, Isabelle: 41
Billard, Patrick: 61
Bittarello, Alis C.: 190
Bilnova, Irina: 129, 160
Bohme, Steffi: 27
Bolaños, Viviana: 214
Bonfim, Larissa: 223
Borch, Thomas: 63
Borisoever, Mikhail: 35, 130
Borschneck, Daniel: 26
Bossa, Nathan: 26
Botero, Wander G.: 155
Bottero, Jean-Yves: 26
Boulimia, Naima: 237
Boylé, Pierre: 120
Boyle, Edward: 134
Bray, Sarah A.: 230
Braeutigam, Patrick: 201
Braga, Camila P.: 190, 191
Brault, Marion: 31
Brendi, Jocelyne: 97, 114
Briesch, Dionir Luiz: 207
Brixas, Enrico: 82, 145
Brown, Andy: 33
Brydson, Rik: 33
Bucheli, Thomas D.: 93
Bukhanovsky, Nadezhda: 35
Buzzi, Claudia: 219
Byrne, Patrick: 188
Cabot, Pere Luis: 145
Campagnolo, Marcelo Angelo: 133, 150, 165, 207
Campbell, Peter G.C.: 58
Cancello-González, J.: 175
Caniego, J.: 249
Cao, Hongbin: 89
Cappuyns, Valérie: 218
Carrasco, Gonzalo: 134
Cavecci, Bruna: 190
Cazzo, Victor Natan: 133
Cecilia, Joan: 158, 244
Centellas, Francesc: 145
Cerbo, Maria R.: 191
Chakraborty, Sudipta: 97
Charlet, Laurent: 94, 97
Chaurand, Perrine: 26
Chavez, A.M.: 47
Chefetz, Benny: 63, 143
Chelarescu, Elena Daniela: 233
Chen, Weibin: 43
Cheng, Hao: 78
Cho, Dong-Wan: 136
Choi, Jiyeon: 135, 240
Chon, Chul-Min: 136, 182
Ciuffi, Katia Jorge: 186, 223, 224, 225
Clark, M. L.: 226
Cleis, Santos: 108
Coasne, Benoit: 70
Coelho, Gustavo Ferreira: 133, 150, 165, 207
Colbea, Claudiu: 200
Companys, E.: 77, 81, 137, 197
Comtat, Maurice: 120
Conradi, Elio: 165
Constantin, Lucian: 185
Cosio, Claudia: 59
Cosma, Cristina: 84
Coulon, Nathalie: 75
Crisan, Maria: 185
Cristea, Ionut: 84, 185
Croue, Jean-Philippe: 24
Cruz-González, S.: 206
Czech, Z.: 209
D’Haese, Arnout: 83
da Silva, Tiago H.: 223
Dachowski, Ryszard: 234, 241
Dago, Angela: 137
Danielsson, Karin: 23
Dao, Thanh H.: 80
Darmograi, Gnaana: 92
Daugelavičius, Rimantas: 214
David, C.A.: 132, 199, 206
David, L.: 141
Davison, William: 78, 158
Dawson, Kenneth A.: 21
de Faria, Emerson H.: 186, 187, 223, 224, 225
de Oliveira, Lilian Karla: 186, 187
de Sagazan, Olivier: 75
de Vos, W.M.: 138
Dechir, S.: 163, 164
Del Campo Estrada, Estefania: 68
Del Nero, Mirella: 64
Delgado, Ángel V.: 90, 110
Delimi, Rachid: 127
Derriére, Zoubir: 159
Dey, R.K.: 52
Dickhout, J.M.: 138
Didier, Pierre: 75
Djemel, Abdelhak: 127
Do, Thi Trang: 51
Dobrojan, Sergiu: 198
Doméngos, Rute F.: 32, 40
Domínguez, Caio Vinicius Ramires: 150, 207
dos Santos, Natália Cardoso: 165
Dragunski, Douglas Cardoso: 150
Index of authors

Saeed, Khalid: 56
Saito, Takumi: 42
Salaru, Vasile: 198
Salaun, Pascal: 74
Saldarriaga Hernandez, L. A.: 54
Selles, Fabrice: 92
Saltarelli, Michelle: 224
Salvadó, Victoria: 250
Samia, Benrabah: 232
San José, F.: 249
Sánchez-Iglesias, Ana: 101
Sander, Michael: 105
Sastre de Vicente, Manuel E.: 169, 173
Sato, Tsutomu: 184
Scheinost, Andreas C.: 97
Schirmer, Kristin: 30
Schlosser, Christian: 96
Schmid, Doris: 152, 153
Schoutteten, Klaas: 83
Schwahn, Dietmar: 247
Schwantes, Daniel: 133, 165, 207
Scifo, Lorette: 26
Sedó, Maria: 81
Sedouci-Bereksi, M.: 238, 239
Sefah, J.: 208, 209, 210, 211
Serra, Olga: 81
Sethi, Rajandrea: 54
Setti, Nawal Drici: 159
Sever-Škapin, A.: 180
Shabtai, Itamar: 91, 212
Sharipova, A.A.: 112, 113
Shi, Cong: 161, 161
Siboulet, Bertrand: 70
Siggelkow, Gabriel: 93, 213
Sihtmäe, Mariliis: 214
Silva, Nelson J.: 191
Silva, Evane: 224
Šimůnek, J.: 230
Sirés, Ignasi: 145
Situm, Arthur: 102
Sivry, Yann: 39
Slaurejko, Vera I.: 59
Smith, D. Scott: 43
Soneda, Yasushi: 142
Song, Myong Shin: 117, 157, 215
Song, Hocheol: 136
Souza, Suelen D.: 187
Stefanescu, Mihai: 84, 185
Stelter, Michael: 201
Stepien, Anna: 234
Stihi, Claudia: 233
Stipp, S.L.S.: 20
Stott, Tim: 188
Strmekci, Sladana: 76
Suchorab, Z.: 195
Sulzberger, B.: 216
Sun, Weiling: 25, 227
Sun, Huichao: 213
Su, Hua: 32
Swain, S.K.: 52
Wu, Mingsheng: 45, 99, 100, 144, 167
Wu, Mingxia: 45, 99, 100
Wang, Conghe: 25
Wang, Changyong: 135, 240
Wang, Zhiyi: 154
Wang, M.: 230
Wang, Wei: 89
Wang, Dan: 170
Wang, Weili: 254
Wang, Ming: 231
Wang, Mingxia: 45, 99, 100
Wang, Ming Kang: 154
Wei, Jingmiao: 227
Wei, Jingming: 62
Wesolowski, David J.: 71
Wilpers, K.: 209
Windmühler, Claudiia C.: 60
Winkel, Lenny H.E.: 37
Wolbert, Dominique: 123
Wong, Kerwin K.W.: 49
Wroblewska, A.: 179, 210
Wu, Yunxia: 73, 229
Xiong, Juan: 45
Xu, Jinling: 45
Yang, Seung Cheol: 135, 240
Yang, Sheng: 235
Yoon, Min-Ho: 182
Yossi, Itamar: 226
Young, Robert B.: 63
Yu, Fangke: 231
Zach, Hafida: 243
Zaib, Qammer: 146
Zajac, Jerzy: 92
Zanane, Chorouk: 243
Zara, Luis F.: 190, 191
Zgrzebnicki, M.: 228
Zhang, Hao: 78, 158
Zhang, Pei: 99
Zhang, Changyong: 106
Zhang, Zhiyi: 154
Zhang, M.: 230
Zhao, He: 89
Zhao, Dan: 170
Zerbe, Christopher: 196
Zimmermann, Juliano: 133
Zimny, Thierry: 235
Practical information

Wireless network setup

To access the wireless network from your laptop, please, choose the wireless network CONGRES.

Once you find and choose the network CONGRES, please, activate an internet browser. Then the following information should be provided:

User: cciap
Password: 2016-IAP

Desktop PCs in Computer Room

User: cciap
Password: 2016-IAP
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