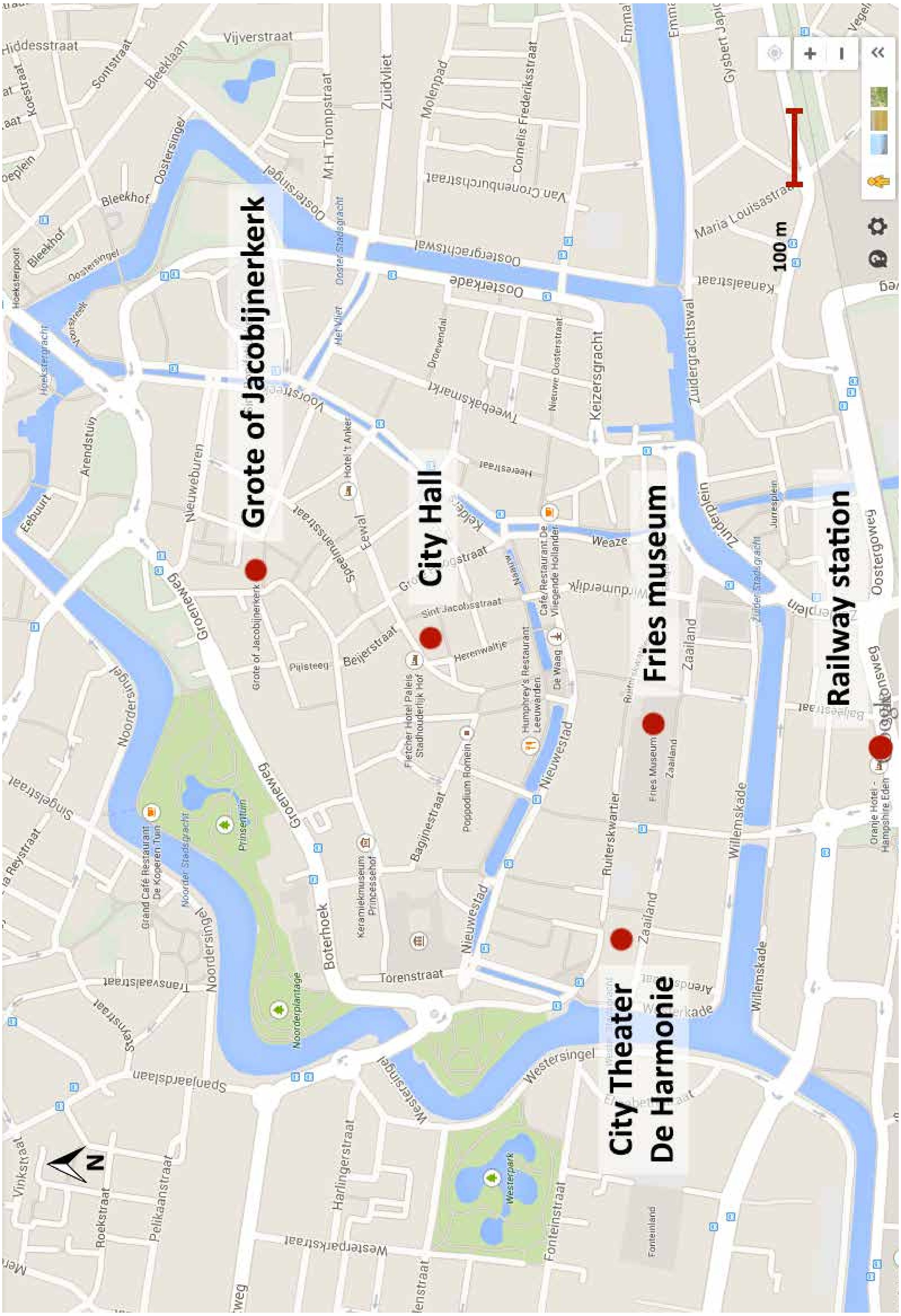
May 26-28, Leeuwarden

IAP 2014

Interfaces in Water and Environmental Science

Wetsus is co-funded by

- the Dutch Ministry of Economic Affairs (IOP-TTI, Peaks in the Delta)
- the Dutch Ministry of Infrastructure and the Environment
- the European Union (European Fund for Regional Development and Seventh Framework Programme)
- Northern Netherlands Provinces (REP-SNN)
- the City of Leeuwarden, the Province of Fryslân and University Campus Fryslân



Leeuwarden, City Center

Welcome

The 8th International Conference Interfaces Against Pollution (IAP2014), held in Leeuwarden, the Netherlands from May 25 to 28, is part of a proud series of conferences initiated in Wageningen (The Netherlands, 1997) and followed in Miskolc (Hungary, 2002), Julich (Germany, 2004), Granada (Spain, 2006), Kyoto (Japan, 2008) , Beijing (China, 2010) and most recently in Nancy.

IAP conferences seek to provide a forum for researchers working in the interdisciplinary field of Environmental Science. Colloids and Interfaces in natural and engineered media are at the heart of the conference. This includes topics of societal concerns like environmental protection, remediation of polluted sites, water treatment, optimization of mineral resources and the impact of nanotechnology residues on the environment.

IAP has a broad, but fundamentally scientific scope, which has broadened over the years. The IAP 2014 specifically has shown to attract a large community in the field of capacitive desalination. In line with the wide spectrum of disciplines (physics, biology, physical chemistry, mineralogy) relevant for environmental science, IAP2014 is intended to cover research from work at the nano-, meso- and macroscopic scales, from transient processes to equilibrium.

The international IAP advisory council and the local IAP2014 organization committee would like to thank our sponsors Gemeente Leeuwarden, Provinsje Fryslân, Wetsus, Water Campus Leeuwarden, Voltea, IACIS and ISE for enabling this conference.

The international IAP advisory board and the local IAP2014 organization committees wish that this conference will be an opportunity for all participants to share fruitful discussions, in Leeuwarden.

Conference chairs

Prof. Dr. David Waite (University of New South Wales, Australia),
Dr. Bert Hamelers (Wetsus, The Netherlands)

Mayor Ferd. J.M. Crone of the City of Leeuwarden, capital of the province of Fryslân:

Welcome to Leeuwarden, the European Capital of Culture 2018!
Leeuwarden is a dynamic city which is situated in a green and water-rich environment.
The city has a watery heart and a heart for water.
The abundance of water is a defining feature of the city’s image and atmosphere. The recovery of water, energy, food and resources has a high priority. In addition, water is an important factor in the research and development of water technology and sustainability. The expansion of the Water Campus Leeuwarden is a good example of this.
I wish you an interesting congress and enjoy your visit to Leeuwarden, the Capital of Water Technology.

About the organization

Conference chairs

Dr. Bert Hamelers
Conference chair
Wetsus, Netherlands

Prof. Dr. David Waite
Chair IAP council
UNSW, Australia

Prof. Dr. Luuk Koopal
Founder of IAP
WUR, Netherlands

Local organizing committee

Dr. Maarten Biesheuvel
co-chair

Prof. Dr. Volker Presser
co-chair

Dr. Jan Post
conference director

Oane Galama

Jouke Dykstra

Hester Henstra

Linda van der Ploeg

Vytautas Abromaitis

Joeri de Valença

Questions?

In case you have questions about general issues, the local organizing committee can help you.
During the conference you can contact them the following ways:

- ask the committee members in person;
- go to the information desk of De Harmonie;
- send an e-mail to iap2014@wetsus.nl (we will answer your mail during the conference);
- call +31(0)6 46 24 70 80

International scientific committee

Yasu Adachi (Japan)
Maarten Biesheuvel (Wetsus, Netherlands, co-chair)
Rob Comans (Wageningen, Netherlands)
Jerome Duval (France)
Bert Hamelers (Wetsus, Netherlands, chair)
Hong He (China)
Guido Mul (Twente, Netherlands)
Volker Presser (INM, Germany, co-chair)
Louis de Smet (Delft, Netherlands)
David Waite (Australia)

International advisory council

Yasuhisa Adachi (Japan)
Marcelo Avena (Argentina)
Philippe Behra (France)
Maarten Biesheuvel (Netherlands)
Michal Borkovec (Switzerland)
Scott Bradford (USA)
Andrzej Dabrowski (Poland)
Angel Delgado (Spain)
Jerome Duval (France)
Menachim Elimelech (USA)
Fernando Gonzalez-Caballero (Spain)
Ellen Graber (Israel)
John Gregory (UK)
Hong He (China)
Stephan Hug (Germany)
Erwin Klump (Germany)
Luuk Koopal (Netherlands)
Nataliya Mishchuk (Ukraine)
Jiuhui Qu (China)
Etelka Tombacz (Hungary)
Raewyn Town (Denmark)
David Waite (Australia)
Kevin Wilkinson (Canada)

Frontpage courtesy J. de Valença “Dynamics of micro-vortices in ion-exchange membranes”

General information

Conference location

The conference location is De Harmonie, Leeuwarden. De Harmonie is Leeuwarden's city theatre, located in the old city centre. Leeuwarden is a beautiful small old and historical city with royal connections and an extensive canal network.

The address of De Harmonie is:
Stadsschouwburg De Harmonie
Ruiterskwartier 4
8911 BP Leeuwarden
The Netherlands

Internet service

There is free wireless internet available in City Theatre de Harmonie.
The following login details are required:

Login:	IAP-congress
Password:	IAP2014

Oral presentations

There are two ways to turn in your oral presentation (.pdf, .pptx, .ppt):
- to e-mail your presentation at least 24h in advance to iap2014@wetsus.nl.
- to hand in your presentation on a flash drive (usb stick, thumb drive) in the morning before start of the program at the central registration desk near the entrance in De Harmonie, not in the conference rooms!

Poster presentations

Please bring your poster to the exhibition floor of De Harmonie (ground floor) from 08.30 - 09.30 on Monday, where we will assist you to put up your poster.

Poster prize award

Besides oral presentations, there is a special poster presentation session. This will be held on Monday 26th of May from 17.00 – 18.00 PM on the ground floor of our conference center: 'De Harmonie'. During this session researchers are given the opportunity to explain to, and discuss about their scientific research topic with the visiting audience. Members of the Poster Prize Committee will assess the quality of the poster and the interaction with interested attendees. The poster prize ceremony will be held during the dinner on Tuesday in De Grote of Jacobijnerkerk.
We wish all participants good luck and fruitful interactions with the attendees.

Questions?

In case you have questions about general issues, the local organizing committee can help you.
During the conference you can contact them the following ways:
- ask the committee members in person;
- go to the information desk of De Harmonie;
- send an e-mail to iap2014@wetsus.nl (we will answer your mail during the conference);
- call +31(0)6 46 24 70 80

Social program

Welcoming reception, Sunday, 17.30, The city hall of Leeuwarden

The conference starts with a welcoming reception in the City Hall of Leeuwarden, Hofplein 38 in Leeuwarden, on Sunday May 25.

Reception, Monday, 18.00, De Harmonie

On Monday after the poster session, there is an Italian style buffet reception at De Harmonie, the City Theatre of Leeuwarden, the conference location of IAP2014.

Conference dinner, Tuesday, 18.30, Grote of Jacobijnerkerk

On Tuesday, there is the Conference Dinner in De Grote of Jacobijnerkerk in Leeuwarden. The location is pointed out on the map, which you can find on the backcover of this conference book. During the conference dinner former president and founder of IAP, Prof. Dr. Luuk Koopal, will share his view on the "past, present, and future of IAP."

***Luuk Koopal** worked at the Laboratory of Physical Chemistry and Colloid Science of Wageningen University, NL. Since 2007 he is Guest Professor at Wageningen University and at the College of Resources and Environment, Huazhong Agricultural University in Wuhan, P.R. China. He has served **IUPAC** as Chairman of the Colloid and Surface Chemistry Commission and as member of the Bio-Physical Chemistry Division and is Past President of the International Advisory Board of the **IAP** conferences. His research interests are: interaction of ions, surfactants and nano-particles with mineral surfaces and humic substances, and their effects on colloid stability, wetting and flotation.*

Visit at Wetsus or Fries museum, Wednesday, 15.00

On Wednesday, at 15.00 PM, there are two optional excursions:
- to the Fries museum, where you can see 170,000 objects of Frisian art, culture and history;
- to Wetsus, where we will show you the laboratory and research facilities.

On Monday, when you register for the conference, you will receive a registration form for these optional excursions. If you like to attend, you can hand in this form before leaving De Harmonie on Monday. Alternatively, you can send an e-mail with your choice to iap2014@wetsus.nl on Monday.

Former conferences

The 8th International Conference on Interfaces against Pollution (IAP) to be held in Leeuwarden (2014), lies within the framework of a series of conferences held previously in:

- Nancy (France, 2012)
- Beijing (China, 2010)
- Kyoto (Japan, 2008)
- Granada (Spain, 2006)
- Jülich (Germany, 2004)
- Miskolc (Hungary, 2002)
- Wageningen (The Netherlands, 1997)

Monday	IAP 1 – Rabobank zaal	IAP 2 – Nivo Noord zaal	CDI Symposium – Bentacera zaal
8.30	Registration desk open and coffee		
9.30-9.40	Welcoming ceremony (**Bert Hamelers, Cees Buisman, David Waite**) (Rabobank zaal)		
9.40-10.20	**Paul Tratnyek** - Oregon Health and Science University, USA - Reactivity of Iron Nanoparticles: Spectroscopy, Electrochemistry, Kinetics, and Environmental Implications (page 14) (Rabobank zaal, chair: Bert Hamelers)		
10.20-11.00	Coffee		
11.00 -12.20	***Catalysis and electrochemistry: carbon materials*** *Chair: David Wesolowski* **Mickaël Gineys** - Reversible trapping of water contaminants on nanoporous carbon electrodes (page 22) **Laurent Duclaux** - Adsorption kinetics and isotherms of micropollutants onto activated carbon fabric and felt (page 23) **Xu Zhao** - Electrochemical reduction of haloacetic acids in a three-dimensional electrochemical reactor with Pd-GAC particles as fixed filler and Pd-modified carbon paper as cathode (page 25) **Yael Mishael** - Developing Efficient Polycation-Clay Sorbents for the Removal of Pharmaceuticals and Dissolved Organic Matter (page 26)	***Adsorption in environmental processes : analytical methods & organic chemistry*** *Chair: Ellen Graber* **Soraya Heuss-Aßbichler** - Mineralogical investigations of precipitates obtained by treatment of Cu-rich waste water by Ferrite process (page 27) **He Zhao** - Cross-coupling oxidation of bisphenol A during electro-enzymatic oxidative process (page 28) **Benedicte Prelot** - Interactions of organic dyes with layered double hydroxides (page 29) **Manuel Nuño** - Study photocatalytic reactions for pollution remediation by electron ionisation mass spectrometry (page 30)	***Processes in CDI*** *Chair: Bert van der Wal* **Xiaowei Sun (k)** - Applications of electrosorption systems for waste water recovery (page 31) **Slawomir Porada (k)** - Electrodes in motion for water desalination and energy harvesting (page 32) **Kelsey Hatzell (k)** - CDI based on flowable electrodes (page 33) **Eran Avraham (k)** - Water desalination by CDI – advantages and limitations (page 34)
12.20-13.00	Lunch		
13.00-13.40	**Hans Lyklema** - Wageningen University, The Netherlands - Models of colloids and models for interpretation. A bit of history. (page 15) (Rabobank zaal, chair: Maarten Biesheuvel)		

13.50-15.10	***Catalysis and electrochemistry*** *Chair: Paul Tratnyek* **Yi-Fan Han (k)** - Free Radicals Generating from Catalytic Decomposition of H_2O_2: New Strategies and Applications (page 35) **Rob Lammertink** - Fast Degradation In Immobilized Photocatalytic Microreactors (page 37) **HansPeter Zöllig** - Fast inhibition of direct ammonia oxidation on thermally decomposed iridium oxide films through a change in local pH (page 38)		***New materials in CDI*** *Chair: Maarten Biesheuvel* **Jieshan Qiu (k)** - Carbon Nanofiber and Graphene Composites made by Electrospinning for CDI (page 39) **Volker Presser** - Effect of pore size and its dispersity of porous carbon on capacitive deionization (page 40) **Chengzhi Hu** - Preparation of a MnO_2/Carbon Composite Electrode for Electrosorptive Removal of Heavy Metal from Water (page 41) **Karthik Laxman** - Zinc oxide nanorods coated carbon electrodes for improved energy efficient CDI of brackish water (page 42)
15.10-15.30	Coffee		
15.30-16.50	***Catalysis and electrochemistry*** *Chair: Huub Rijnaarts* **Nora Sutton** - Geochemical and microbiological characteristics during in situ chemical oxidation and in situ bioremediation at a diesel contaminated site (page 43) **Loes Fasotte** - Removal of MTBE from groundwater by adsorption and catalyzed ozonation (page 44) **Elena Mejia Likosova** - An Innovative 2-Stage Process for the Recovery of Phosphorus and Recycling of Ferric from Ferric Sludges Generated in Water and Wastewater Treatment (page 45)	***Adsorption in environmental processes: analytical methods & organic chemistry*** *Chair: Yi-Fan Han* **He Jie** - Heterogeneous Fenton oxidation of catechol and 4-chlorocatechol catalyzed by nano-magnetite: role of the interface reaction (page 46) **Julien Muller** - Synthesis and complexation properties of new polyvinyl alcohol (PVA)-based chelating polymers (page 47) **Gaelle Gassin** - Non linear optical tools to study ions remediation processes (page 48) **Jie Ye** - Preparation of γ-AlOOH loaded-zeolites and characteristics for phosphate adsorption (page 49)	***Applications of CDI*** *Chair: Jieshan Qui* **Jihun Kim** - Removal efficiency of high concentration waste water using Capacitive Deionization Process (page 50) **Alexandra Rommerskirchen -** Batch mode and continuous membrane capacitive deionization using flowing carbon electrodes (page 51) **Patrick Curran** - Hyper Salinity Desalination using Atlantis RDI Capacitive Deionization Technology (page 52) **Cleis Santos Santos** - Capacitive Deionization for Waste Water Re-use: Energy Efficiency Considerations (page 53)
17.00-18.00	Poster session + drinks		
18.00-19.30	Reception		

Tuesday	IAP 1 – Rabobank zaal	IAP 2 – Nivo Noord zaal	CDI Symposium – Bentacera zaal
8.30	Coffee		
9.00-9.40	**Michael Sander** – ETH Zürich, Switzerland – Should I stay or should I go now: assessing electron transfer properties of organic and mineral phases using analytical electrochemistry (page 16) (Rabobank zaal, chair: David Waite)		
9.50-11.10	***Adsorption to engineered surfaces*** *Chair: Alberto Tiraferri* **Ellen Graber** - Role of Surfaces in the Biochar Effect (page 56) **John Gregory** - Phosphate adsorption on hydrous ferric oxide and its effect on the re-growth of broken flocs (page 57) **Dung Viet Pham** - Effect of phosphate sorption on Ferralsol dispersion: Evaluation with stability ratio and repulsive potential energy (page 58) **Behnam Akhavan** - Plasma Polymer Coated Particles: A New Class of Adsorbents for Water Purification (page 59)	***Transport and mass transfer at interfaces*** *Chair: Amy Tsai* **Luewton L. Agostinho (k)** - Characterization of droplets produced by electrospray emulsification (page 60) **Norbert Kuipers** - Simultaneous production of high quality water and electrical power from aqueous feedstocks and waste heat by high pressure membrane distillation (page 61) **Krzysztof Trzaskus** - Investigating the fouling stages during membrane filtration of silica nanoparticle solutions (page 62) **Maike Gröschke** - Transport of Sewage-borne Ammonium in a Floodplain Aquifer: Column Experiments with Aquifer Materials from the Yamuna Floodplain in Delhi (India) (page 63)	***Desalination*** *Chair: Bert Hamelers* **Frieder Mugele** - Ion adsorption at mineral-electrolyte interfaces probed by high resolution Atomic Force Microscopy (page 64) **Thomas Sweijen** - Pore-scale study of processes and transport in porous media; an overview (page 65) **Joeri de Valenca** - The Dynamics of Micro-vortices During Overlimiting Electrodialysis (page 66) **Sven Schlumpberger** - Water Purification and Brine Concentration by Shock Electrodialysis (page 67)
11.10-11.40	Coffee		
11.40 -13.00	***Adsorption to engineered surfaces*** *Chair: Rob Lammertink* **Helene Fallou** - Dynamic adsorption of pharmaceutical residues at trace concentrations onto activated carbon cloths (page 68) **Alberto Tiraferri** - Adsorption of chitosan from aqueous solutions onto silica (page 69) **Shazia Ilyas** - Sacrificial polymer layers for easy membrane cleaning (page 70) **Yasuhisa Adachi** - Colloidal flocculation of PSL particle induced by an adsorption of polyelectrolyte studied in relatively concentrated suspension (page 71)	***Transport and mass transfer at interfaces*** *Chair: Luewton L. Agostinho* **Norazanita Shamsuddin** - Effects of MF membranes deformation and permeability on filtration of clay suspension and its solution chemistry (page 72) **Stylianou Stylianos** - Modified Hydrophobic Ceramic Membranes: Use For Ozone Transfer To Water (page 73) **Barbara Liszka** - A pneumatic micro-fluidic device for in-situ detection of mineral scaling at a membrane surface (page 74) **Amy Tsai** - Momentum and mass transport over a superhydrophobic bubble mattress: the influence of interface geometry (page 75)	***Capmix / New materials*** *Chair: Slawomir Porada* **Angel Delgado** - Temperature effects on energy production by salinity exchange (page 76) **Lorenza Misuri** - Functionalized activated carbon for "capacitive mixing" energy production (page 77) **Sangho Chung** - Ultrathin metal oxide coated mesoporous carbon material for enhanced capacitive deionization (page 78) **Jianyun Liu** - Mesoporous carbon nanofiber fabrication and its capacitive desalination application (page 79) **Park Namsoo** - CDI carbon electrode coated with ion selective layer (page 80)

13.00-14.00	Lunch		
14.10-14.50	**Akram Alshawabkeh –** Northeastern University, Boston, USA - Electrochemical transformation of contaminants – electrode interface and beyond (page 18) (Rabobank zaal, chair: Raewyn Town)		
15.00-16.20	***(Bio-)polymer/water interaction and charge effects*** *Chair: Luuk Koopal* **Jerome Duval (k)** - Dynamics of metal uptake by biointerfaces (page 81) **Oane Galama** - Validity of the Boltzmann equation to describe Donnan equilibrium at the Membrane-Solution Interface (page 82) **Josep Galceran** - Recent advances in diffusive gradients in thin films (DGT). The role of electrostatic effects and dissolution of metal nanoparticles (page 83) **Louis de Smet -** Capacitive Response of PDMS-coated IDE Platforms Directly Exposed to Aqueous Solutions Containing Volatile Organic Compounds and Salts		***New materials in CDI / characterization of CDI*** *Chair: Volker Presser* **Jeyong Yoon (k)** - The importance of carbon electrode material affecting the maximum deionization performance in CDI process (page 85) **Li-Ching Chung** - Insight in TiO2/AC electrodes prepared by a microwave-assisted ionothermal synthesis method for CDI (page 86) **Heena Mutha** - Vertically-Aligned Carbon Nanotube Electrodes for CDI (page 87) **Florian Schipper** - The Influence of Heteroatom Doping of Porous Carbon on the Salt Adsorption Capacity and Kinetics in CDI (page 88) **Yatian Qu** - Characterization of Internal Resistance for Capacitive Deionization Systems (page 89)
16.20-16.50	Coffee		
16.50-17.50	***(Bio-)polymer/water interaction and charge effects*** *Chair: Michael Sander* **Luuk Koopal** - Protein humic acid interaction (page 90) **Elise Rotureau** - A biophysicochemical approach for assessing the dynamics of metal uptake by microorganisms (page 91) **Mikhail Borisover** - Sorption of organic molecules on environmental sorbents: driving water molecules in or out? (page 92)	***Case studies, transport and conversion*** *Chair: Oane Galama* **Yassine Bentahar** - Comparison of Arsenic Adsorption on clays from Morocco (page 93) **Juan Antelo** - Attenuation of metal cations by iron oxide minerals from acid mine drainage (page 94) **MA Weifang** - Adsorption and aerobic biodegradation of three selected endocrine disrupting chemicals in artificial groundwater recharge with treated reclaimed municipal wastewater (page 95)	***Characterization of CDI*** *Chair: Jouke Dykstra* **Chia-Hung Hou** - Study of Electrosorption Performance of Nanostructured Carbon Electrodes in CDI (page 96) **Doo-Hwan Jung** - Pore-structure of Activated Carbon Fibers on CDI (page 97) **James Landon** - Capacitive Deionization with PZC-Modified Carbon Xerogel: Half-Cell and System Analysis for Long-Term Operation (page 98)
18.30	Dinner in De Grote of Jacobijnerkerk (location indicated on the map, which you can find on the back cover of this book)		

Wednes-day	IAP 1 – Rabobank zaal	IAP 2 – Nivo Noord zaal	CDI Symposium – Bentacera zaal
8.00	Coffee		
8.30-9.10	**Liane Benning –** University of Leeds, UK - The Birth and Life Cycle of a Nanoparticle or how to make crystals from ions (page 19) (Rabobank zaal, chair: Erwin Klumpp)		
9.20-10.40	***Adsorption in environmental processes: Interaction and processes*** *Chair: Yasuhisa Adachi* **Romain Dagnelie** - Diffusion Of Anthropogenic Organic Matter In Clay Rock (page 100) **Olga L. Gaskova** - Uranium migration at nuclear waste management facilities: experimental versus thermodynamic modeling (page 101) **Munehide Ishiguro** - Adsorption of sodium dodecylbenzene sulfonate in highly humic volcanic ash soil (page 103) **Salini Sasidharan** - Coupled Effects of Hydrodynamic and Solution Chemistry Conditions on Long-Term Nanoparticle Transport and Deposition in Saturated Porous Media (page 104)	***Nanoparticles, materials, effects, transport*** *Chair: Philippe Behra* **Mieke Kleijn** - Coverage and disruption of phospholipid membranes by oxide nanoparticles (page 105) **Wenfeng Tan** - Shape evolution synthesis of crystalline hematite (α-Fe_2O_3) nanoparticles using ascorbic acid and tartaric acid (page 106) **Toshio Sakai** - Removal of organic pollutants from water by TiO_2/CnTAB Nanoskeleton (page 107) **Stéphane Daniele** - Smart Hybrid Nano-Composite Devices for Removal of PAH Micro-pollutant from Wastewaters (page 108)	***Theory of CDI*** *Chair: Matthew Suss* **Mathijs Janssen** - Temperature and size effects on the desalination of water (page 109) **Andreas Haertel** - Structural and size effects on the desalination cycle of water (page 110) **Maarten Biesheuvel** - Membrane CDI: definitions, and double layer modeling (page 111) **Dennis Cardoen** - Multiphysics simulation of Membrane CDI for mixed streams (page 112) *Announcements CDI conferences 2015, 2016*
10.40-11.10	Coffee		

11.10 -12.10	***Adsorption in environmental processes: Interaction and processes*** *Chair: Mieke Kleijn* **Jerome Labille** - Is solution chemistry responsible for clay particle mobility through soil pores? (page 113) **Chen Yang** - Sorption of tylosin on goethite (page 114) **Philippe Behra** - Effect of pyrite interface on silver and mercury behavior in natural porous media (page 115)		***Processes in CDI*** *Chair: James Landon* **Matthew Suss (k)** - Flow-through electrode CDI and experimental characterization of desalination electrodes (page 116) **Jouke Dykstra** - Enhanced energy efficiency in increased discharging voltage Capacitive Deionization (page 118) **Sung-il Jeon** - Seawater Desalination and Energy Recovery using Flow-electrode Capacitive Deionization (FCDi) (page 119)
12.10-13.10	Lunch		
13.10-14.10	***Adsorption in environmental processes: Interaction and processes*** *Chair: Jerome Duval* **Raewyn Town** - Labilities of aqueous nanoparticulate metal complexes (page 120) **Yonatan Keren** - Wastewater effects on soil-organic compound interactions, non-typical sorption isotherms and clay vs. SOM as sorbing phases (page 121) **Liping Weng** - Arsenic Adsorption: Effect of pH, Natural Organic Matter and Oxides Composition (page 122)	***Nanoparticles (materials, effects, transport)*** *Chair: Liane Benning* **Erwin Klumpp** - Retention and Remobilization of Stabilized Silver Nanoparticles in Soils (page 123) **Sondra Klitzke** - The role of soil-borne DOC on the aggregation of synthetic Ag nanoparticles in soils (page 124) **David Waite** - Silver nanoparticle-based water treatment: mechanistic aspects and technology viability (page 125)	***Processes in CDI*** *Chair: Xiaowei Sun* **Gang Wang** - Ultrasound-assisted Preparation of Electrospun Carbon Nanofiber/graphene Composite electrode for CDI (page 126) **Qinghan Meng** - CDI of NaCl solution using activated carbon electrodes in a novel CDI module (page 127) **Bert van der Wal (k)** – Salt removal, water recovery and energy consumption in Membrane CDI (page 128)
14.10-14.50	**David Wesolowski** – Oak Ridge National Laboratory, USA - The Oxide-Water interface, Neither Oxide Nor Water! (page 20) (Rabobank zaal, chair: Volker Presser)		
14.50-15.00	Closing ceremony IAP 2014 (Rabobank zaal)		
15.00	Excursions to Wetsus or Fries Museum. In case you signed up for one of the excursions, please gather outside De Harmonie, near the entrance.		

INVITED PLENARY LECTURES

Reactivity of Iron Nanoparticles: Spectroscopy, Electrochemistry, Kinetics, and Environmental Implications

Paul G. Tratnyek

Institute of Environmental Health, Oregon Health & Science University, 3181 SW Sam Jackson Park Road, Portland, Oregon 97239-3098 USA, Email: tratnyek@ohsu.edu, Web: http://www.ebs.ogi.edu/faculty/tratnyek.html

In the early 1990s, permeable reactive barriers (PRBs) containing zero-valent iron (ZVI) emerged as a reliable and cost-effective technology for remediation of groundwater contaminated with chlorinated solvents. Since then, the range of ZVI applications in treatment processes has expanded to include other classes of organics (e.g., energetics, pesticides, dioxins, etc.), many metals (As, Cr, Se, etc.), other inorganics (nitrate, residual chlorine), acid mine drainage, and possibly even some pathogens.

In parallel with the diversification of engineering applications, a large body of scientific literature has developed on many aspects of treatment processes based on ZVI (and other zerovalent metals). This is partly because granular ZVI in aquatic media has become a favorite model system for investigating many aspects of interfacial redox processes in the environment. Some of these results are specific to the chemistry of Fe^0, but many are representative of the (bio)geochemistry of ferrous/ferric iron in the environment as a whole.

In our recent work, we have focused on the role that surface layers of organics, oxides, and sulfides play in controlling the overall reactivity of granular ZVI with contaminants from the solution phase. Of particular interest is the coupling between the dynamics of surface layer transformations (e.g., “aging”) and the kinetics of reactions between the particles and solutes. Different aging effects apply to different timescales - from seconds to months - and we have found important effects across this whole range, often arising in combinations.

For characterizing interfacial redox processes over diverse timescales, we have found electrochemical methods to be especially valuable. In order to study granular ZVI with its native - or in situ generated - surface coatings, we use packed powder disk electrodes (PDEs) with electrochemical methods developed for studying passive film effects on corrosion of metallic iron. Using powders consisting of a single phase (e.g., high purity micron- or nano-sized ZVI with its native oxide coating), the results obtained by our methods are usually readily interpretable in terms of established corrosion electrochemistry.

In our most recent work, however, we have expanded the application of this approach to multiphase particulate materials. One example is nano ZVI exposed to sulfide, which creates iron sulfides, which improve the sequestration of technetium (as the technetium sulfide). Another example is nano ZVI amended with a range of metals that create authigenic phases by reduction, adsorption, and/or coprecipitation. Interpretation of the data from these systems can be challenging, but some of these challenges can be overcome by various sorts of modeling or meta-analysis. This presentation will highlight results from several recent studies using electrochemical methods to characterize interfacial redox processes involving multi-phase materials containing ZVI. In some cases, it may be necessary to interpret the surface reactivity if the component phases as a product of the overall electrochemical properties of the packed bed as a whole.

Paul Tratnyek is a Professor in the Division of Environmental and Biomolecular Systems and Institute of Environmental Health, at the Oregon Health & Science University (Portland, OR, USA). Previously, he served as a National Research Council Postdoctoral Fellow at the U.S. Environmental Protection Agency Laboratory (1988, Athens, GA, USA), and as a research associate at the Swiss Federal Institute for Water Resources and Water Pollution Control (1989-1991, Zurich, Switzerland). His research concerns the physico-chemical processes that control the fate and effects of environmental substances, including minerals, metals (for remediation), organics (as contaminants), and nanoparticles (for remediation, as contaminants, and in biomedical applications). He obtained his Ph.D. in Applied Chemistry from the Colorado School of Mines in 1987 (Golden, CO, USA). Before, he obtained his B.A. (1980) in Biochemistry at the Williams College (Williamstown, MA, USA).

Models of colloids and models for interpretation. A bit of history.

Hans Lyklema

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People like models, intentionally or subconsciously. For professional colloid scientists it is not different. Over the past century a range of model colloids and a series of model interpretations have been developed and discarded, many of them leaving relevant contributions to our insight. Some of these model substances are still relevant for IAP, for example insoluble oxides and clay minerals. Similarly, theories for interpreting particle interaction have been polished and extended and subjected to increasingly sophisticated measuring methods. For illustration, DLVO theory for the stabilization of lyophobic colloids underwent a number of extensions, its application was widened as a result of the advent of AFM techniques. Looking at the histories of these developments, it is surprising how much insights, obtained with embryonic theories and less-sophisticated instrumentation, have left a lasting influence on our knowledge and thinking.

In the presentation some prominent historical illustrations with their present-day extensions will be reviewed.

Perhaps the oldest illustration of utilizing colloids for the understanding of general physical chemistry was Perrins work of using gamboge mastic colloids and laborious particle counting to assess Avogadro's number. This work is about a century old. However, the method persisted in that from the nineteen seventies onward sols of well-defined colloids were used as models for the structure of condensed liquids.

Model substances for the study of colloid stability started with a variety of natural materials, of which examples can be found in the older editions of Freundlich's Kapillarchemie, also a century ago. Notable progress has been made by Kruyt and others of the Utrecht School by using silver iodide as their model substance. This choice was a lucky strike because silver iodide is chemically rather stable, its charging mechanism by adsorption of charge-determining ions was exemplary, stable sol are relatively easily prepared, stabilities could eventually be measured and silver iodide electrodes made. A number of insights obtained with this system are still important but tend to be forgotten, like the inverse coupling of the influence of indifferent electrolytes on the surface charge and on the sol stability and the origin of ion specificity.

After the silver iodide came the thin liquid films, the homodisperse latices, ludox, and other well-defined colloids displaying interesting macroscopic phase behaviour. Micro-emulsions deserve special mentioning because they are thermodynamically stable and homodisperse.

More recently, models with sterically stabilized particles are becoming popular. Till about 1950 no good theories for these systems existed. Another important branching was stability in media of very low dielectric permittivity.

In real experiments, in addition to trying to achieve maximum experimental information, it is always useful to subject these data to thermodynamic analysis. For this, mostly well-defined and reproducible data are needed, but as thermodynamics are phenomenological, their application may help against overinterpretation of models. In some situations surprising new insights can be obtained. A typical elaboration is obtaining ionic components of charge in electric double layers, that is, splitting the countercharge into the part by positive adsorption of counterions and the contribution of negative adsorption of co-ions. In the presentation this option will be elaborated.

Hans Lyklema is since 1995 Emeritus Professor Physical and Colloid Chemistry in the department of Agrotechnology and Food Sciences at the Wageningen University. He was Professor from 1962-1995 in this department, after starting his scientific career as scientific co-worker and lecturer at the University of Utrecht (1958-1961, Utrecht, The Netherlands). His specialization are colloid and interface science, interfacial electrochemistry, adsorption phenomena, proteins at interfaces, and electrokinetics. Besides many publications and several books, he is the author of: "Fundamentals of Interface and Colloid Science", Vol. I-V. Dr. Lyklema completed the Study Chemistry and Physics (1948-1955), at the State University Utrecht, where in 1956 he received his Ph.D. degree.

Should I stay or should I go now: Assessing electron transfer properties of organic and mineral phases using mediated electrochemical analysis

Michael Sander

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Electron transfer to and from organic and mineral phases plays a key role in many important biogeochemical redox reactions and in pollutant transformation reactions, in both natural and engineered systems. As a consequence, considerable research efforts in numerous disciplines have been directed towards characterizing the redox properties and reactivities of major redox active phases, including dissolved and particulate organic matter (OM), iron-bearing clay minerals, and iron and manganese (oxyhydr-)oxides. Advances towards a concise understanding of the redox properties were, however, challenged by a lack of suitable characterization methods. Most studies had to rely indirect wet chemical approaches. For example, the redox states of OM samples were commonly determined by quantifying the number of electrons transferred from OM samples to added bulk chemical oxidants (e.g., by monitoring the formation of Fe^{2+} following the addition of a complexed Fe^{3+} species to the OM). Other studies employed electrochemical approaches. These, in principle, allow for a more direct assessment of the redox properties and reactivities of organic and mineral phases: in amperometric measurements, electron transfer to and from the phases can be directly monitored via reductive and oxidative currents, respectively, between the phases and the working electrodes of electrochemical cells. In potentiometric measurements, the reduction potential E_h of the geochemical phases can be monitored via redox electrodes. However, many of the amperometric and potentiometric measurements in past work showed kinetic artifacts as a result of extremely slow electron transfer and E_h equilibration between the geochemical phases and the working electrodes.

This contribution focuses on mediated electrochemical analysis, a novel approach that we recently developed to characterize redox-active geochemical phases. The *first part* of the presentation will introduce mediated electrochemical analysis and present some of the results obtained from applying this approach to a diverse set of OM samples and to selected Fe-containing minerals. In mediated electrochemical analysis, dissolved redox mediators are used to facilitate electron transfer and E_h-equilibration between the geochemical phases and the working electrodes in amperometric and potentiometric measurements, respectively (Figure 1). An overview of suitable redox mediators will be given that can be used in measurements over a wide range of reduction potentials from E_h= +0.70 V to –0.54 V (vs. SHE, pH 7). It will be demonstrated how mediated electrochemical reduction and oxidation, two amperometric techniques, can be used to directly quantify the number of electrons that are transferred to and from organic matter and Fe-containing phases at defined E_h and pH conditions in electrochemical cells. Several unique advantages of mediated electrochemical analysis over previous wet chemical approaches will be discussed, including the possibility to analyze particulate organic and mineral phases and to obtain information on both the kinetics and thermodynamics of electron transfer to and from these phases. The first part of the presentation will end with an outlook on the broad application domain of mediated electrochemical analysis.

Michael Sander is a senior scientist in Environmental Chemistry at the Swiss Federal Institute of Technology (Zurich, Switzerland), where he previously held the positions of postdoctoral associate (2005-2007) and research group leader (2008-2013). The work of his group aims at providing mechanistic insights into various physicochemical processes in soil and aquatic environments. The three focus areas of research are environmental analytical electrochemistry and electron transfer reactions, environmental macromolecular chemistry, and the environmental fate of organic micropollutants. In 2005 he received his Ph.D. in Chemical & Environmental Engineering from Yale University (New Haven, USA). Before, he obtained his B.E. (1997) and M.Sc. (2000) in Geoecology at the University of Bayreuth, (Bayreuth, Germany) and an M.Sc. (2002) in Chemical & Environmental Engineering at Yale University.

In the *second part* of the presentation the unique capabilities of mediated electrochemical analysis will be highlighted by selected results of two mechanistic laboratory studies on the redox dynamics of dissolved organic matter (DOM) in temporarily anoxic wetlands. In the first laboratory study, we used mediated electrochemical analysis to quantify changes in the redox states of four different DOM samples over three successive cycles of DOM reduction by *Shewanella Oneidensis* MR-1 under anoxic conditions and subsequent re-oxidation of the reduced DOM by O_2 under oxic conditions. Electron transfer to and from the four DOMs was found to be fully reversible over the three cycles of microbial reduction and O_2 re-oxidation. These findings demonstrate that DOM is a regenerable terminal electron acceptor for anaerobic microbial respiration in temporarily anoxic wetlands. Mediated potentiometric measurements revealed that the four tested DOMs accepted electrons over wide reduction potential ranges and that *Shewanella Oneidensis* MR-1 reduced the DOMs to comparable E_h, suggesting that the extents of microbial DOM reduction were controlled by system thermodynamics. Some of the implications of reversible and sustainable electron transfer to and from DOM for wetland carbon cycling will be highlighted, including the competitive suppression of methanogenesis in these systems by using OM instead of CO_2 as terminal electron acceptor in anaerobic microbial respiration. In the second laboratory study, we used mediated electrochemical analysis to follow the enzymatic oxidation of phenolic moieties in DOM during incubation with phenoloxidases (i.e., laccases). The electrochemical analysis revealed fast, extensive and highly irreversible oxidation of phenolic moieties in DOM by laccase. Furthermore, coupled quantification of DOM oxidation and O_2 reduction by the laccases provided evidence that the initial oxidation of the phenolic moieties in the DOM is followed by coupling reactions that result in the new-formation of electron donating phenolic moieties. The implications of enzyme-mediated oxidation of phenolic moieties in DOM will be discussed in the context of the ‘enzymic latch hypothesis’ that suggests that the activity of phenoloxidases in northern peatlands is a key factor that controls carbon storage in and CO_2 emissions from these systems.

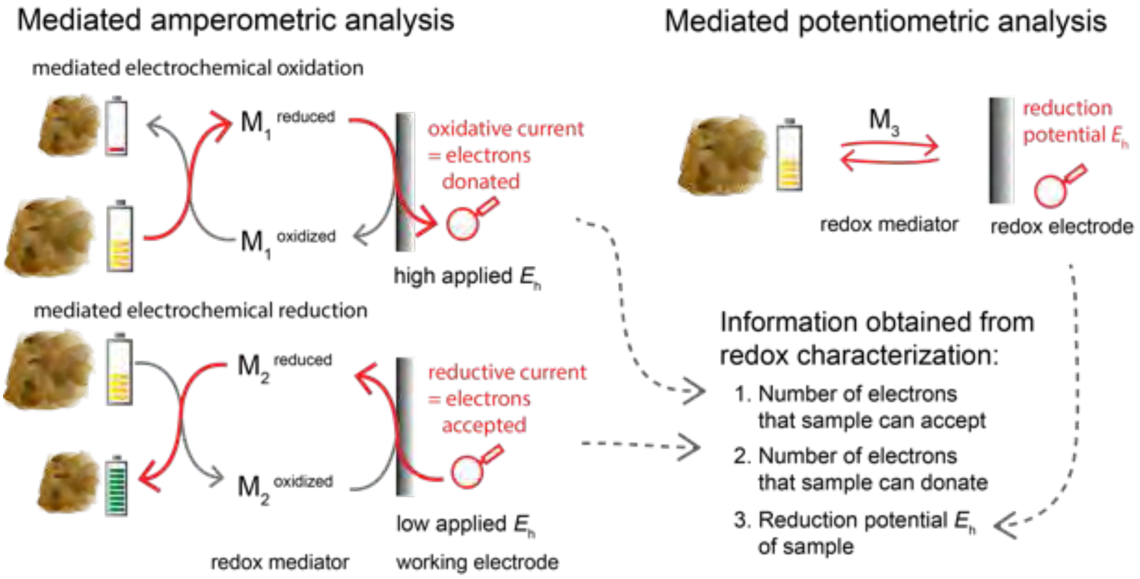

Figure 1 Schematic of mediated electrochemical analysis of a natural organic matter sample in which soluble redox mediators (M) are used to facilitate attainment of redox equilibrium between the phase and the working electrode of the electrochemical cell. Mediated amperometric analysis includes mediated electrochemical oxidation and reduction which allow for a direct quantification of the numbers of electrons that can be transferred from and to the sample at controlled potentials Eh applied to the working electrodes. Mediated potentiometric analysis allows determining the reduction potential Eh of the samples.

Electrochemical transformation of contaminants – electrode interface and beyond

Akram N. Alshawabkeh

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Professor of Civil and Environmental Engineering

PI/Co-Director, PROTECT Center (http://www.northeastern.edu/protect/)

Groundwater contamination is a significant problem in the US, despite three decades of considerable progress in the cleanup of contaminated sites. The most problematic sites are those with potentially persistent contaminants, including chlorinated solvents, and with hydrogeologic conditions characterized by large spatial heterogeneity or the presence of fractures. Remediation costs are significant; it is estimated that the cost for complete closure of Superfund facilities that significantly threaten public water supply systems (estimated at 10% of Superfund sites) is at least $110 billion. The US EPA estimated that the cost over the next 30 years to mitigate these hazards will be more than $209 billion. Inaction may be even more costly, as groundwater contamination can cause poor health outcomes and result in a greater need for expensive healthcare, taxing our already overburdened system. Our long-term goal is to develop novel, sustainable, solar-powered and environmentally-friendly technologies for remediation of contaminated groundwater. We use low direct electric currents through electrodes in wells to manipulate groundwater chemistry by electrolysis. Our target contaminants are chlorinated solvents, specifically trichloroethylene (TCE), but the process is also designed to treat a mixture of contaminants. Two specific transformation mechanisms are evaluated: electrochemical induced reduction and induced chemical oxidation. Although oxidation occurs at the anode, we demonstrated that chemically-reducing conditions can be developed in groundwater using iron anodes, and that the pH and redox potential are optimized using multiple electrodes with controlled current and/or polarity reversal. In contrast to the oxygen-releasing inert anode, the iron anode generates ferrous species, which regulate the electrolyte to a reducing condition (low Oxidation-Reduction Potential or ORP value) and favor the reduction of TCE. The system results in up to 99% dechlorination of TCE with copper foam cathodes. The main products include ethene and ethane; chlorinated intermediates such as cis-DCE or VC are no longer detected. Furthermore, the ferrous species generated from the iron anode can reduce and/or co-precipitate certain aqueous contaminants, such as dichromate, selenate and phosphate. We further evaluated *in situ*-induced chemical oxidation of TCE in simulated groundwater by electro-generated H_2 and O_2 using inert anodes in the presence of Pd and Fe(II). A three-electrode column, one anode and two cathodes, is employed to automatically develop a specific pH condition in the Pd vicinity and a natural effluent. By packing Pd/Al_2O_3 pellets, the column efficiency for TCE oxidation increases with increased Fe(II) concentration. Oxidation removes 95% of TCE within 80 min, and the product distribution proves that the degradation pathway shifts from 79% hydrodechlorination in the absence of Fe(II) to 84% oxidation by •OH in the presence of Fe(II). We demonstrate that in hybrid electrolysis, sulfite at concentrations less than 1 mM greatly increases TCE oxidation by the production of $SO_4^{\bullet -}$, a strong oxidizing radical, and more •OH. In contrast to Pd-catalytic hydrodechlorination under reducing conditions, using a hybrid electrolysis and Pd-catalytic oxidation process is advantageous in controlling the fouling caused by reduced sulfur compounds because the *in situ* generated ROS, i.e., O_2, H_2O_2 and •OH, can oxidize sulfur. A major advantage of electrochemically-generated oxidation or reduction is the ability to regulate pH/redox and develop multiple or sequential reactive zones using multiple electrodes for treatment of a mixture of contaminants within a treatment unit.

Akram Alshawabkeh is a Professor in the department of Civil and Environmental Engineering at Northeastern University (Boston, USA), at which he previously was assistant Professor (1997-2002) and associate Professor (2002-2007). He is also the Director of the PROTECT Center. His fields of expertise are: soil and groundwater remediation, electrokinetic and electrochemical processes, contaminant fate and transport environmental restoration and environmental restoration. In 1994 he received his Ph.D. in Civil and Environmental Engineering from the Louisiana State University. Before, he obtained his B.E. (1998) in Civil Engineering at the Yarmouk University (Irbid, Jordan), and his M.Sc. (1990) in Civil Engineering at the Jordan University of Science and Technology (Irbid, Jordan).

WED 8.30 - 9.10
RABOBANK ZAAL

The Birth and Life Cycle of a Nanoparticle or how to make crystals from ions

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The reactions that control the nucleation, growth and crystallization of mineral phases from solution usually follow a series of complex and often multi-stage reactions that can be slow or extremely fast and that are thus difficult to assess with conventional techniques. However, novel sample preparation / handling approaches, combined *in situ* and time resolved methods (both conventional and synchrotron-based) as well as new developments in with high-resolution imaging permits now such reactions to be quantified at more realistic chemical and physical conditions. These can now span and address important environmental problems (i.e., pollutant remediation, carbon capture and storage) but they also help and are applicable to improving various industrial processes (i.e, reducing mineral scale formation; novel functional materials etc.).

I will discuss how using synchrotron scattering and diffraction methods at high temporal resolution allows now for the nucleation, growth and crystallization pathways for various mineral phases to be evaluated very precisely. I will address the formation of poorly ordered and nanocrystalline phases (i.e., amorphous silica [1], amorphous calcium carbonate [2], and nano-crystalline calcium sulphate [3] or iron sulphide [4] phases) and their crystallization into stable phases (e.g., $CaCO_3$ [5], or $CaSO_4 \bullet 2H_2O$ [3]). I will demonstrate that only through a combination of such *in situ* solid phase analyses with simultaneous monitoring of changes in the reacting solvents (e.g., redox, pH, ion concentrations and speciation), and with high-resolution imaging and micro-spectroscopy characterization of the solids can we realistically derive meaningful mechanism, kinetics and energetics of the relevant reactions.

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Liane G. Benning is a Professor in Experimental Biogeochemistry at the University of Leeds (UK). In 1995 she received her Ph.D. in Aqueous Geochemistry from the Swiss Federal Institute of Technology, (Zurich, Switzerland) after which she worked as a postdoctoral fellow (1996-1999) in the Department of Geosciences at Pennsylvania State University (State College, USA). Her research addresses geochemical reaction mechanisms at low to hydrothermal temperatures in inorganic and biologic systems. In this research she uses a variety of conventional and synchtrotron-based laboratory methods, but also some field approaches to study biogeochemical processes at the molecular level. She obtained her Diploma in Petrology/Geochemistry (1990) and completed her B.Sc. in Marine Geology/Metamorphic Petrology at the University of Kiel (1987, Germany).

The Oxide-Water interface, Neither Oxide Nor Water!

David J. Wesolowski

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In the Geochemistry and Interfacial Sciences Group at Oak Ridge National Laboratory, and in collaboration with Argonne National Laboratory and a number of university partners, we integrate neutron and synchrotron X-ray scattering and spectroscopies with multiscale computational models to reveal the structural, dynamic and reactive properties of aqueous solutions at their interface with minerals. The interfacial region is where all sorption, dissolution, precipitation and surface-catalyzed reactions take place, and the equilibria and kinetics of these processes are profoundly altered by the unique structural and dynamic properties of both the fluid and the mineral surface in the nanoscale interfacial region (Figure 1). Intensive investigations, summarized in over 40 publications, of water and brine interactions with model minerals, including calcite ($CaCO_3$), barite ($BaSO_4$), quartz (SiO_2), rutile (α-TiO_2) and cassiterite (SnO_2), reveal general characteristics of this critical interfacial region, that will be the focus of this presentation. As shown in Figure 1, the structure of water at the interface with an archetypical metal oxide surface, rutile (110) is very different from the 3D H-bonding structure of bulk water. The oxygen density at the interface oscillates wildly, both parallel and perpendicular to the surface, and even the Ti and O atoms of the crystal surface are shifted from their lattice positions (e.g. Zhang et al., 2004, 2007; Predota et al., 2013) in a dynamic manner dependent on the nature of sorbed and intact or partially dissociated water at the underbonded crystal termination. Our extensive molecular dynamics and quasielastic neutron scattering studies of water at oxide surfaces (summarized for rutile by Wesolowski et al., 2012) furthermore demonstrate that interfacial 'water' not only exhibits non-bulk-like densities, but also liquid-like diffusional dynamics down to temperatures more than 100 K below the freezing point of bulk water. This is not a metastable 'supercooling' effect, but rather a consequence of the observation that interfacial water is not the same substance as bulk water, at least within a few nanometers of mineral and oxide surfaces. The interfacial fluid structure and dynamics also control the transport and sorption of dissolved species, due to the competing affinities of these solution constituents for interaction with surface atoms, the highly altered interfacial water, and the hydration spheres around the dissolved species. Furthermore, the presence of water and its dissociated protons and hydroxyl groups at the surface constitute Nature's most abundant and ubiquitous 'capping agents' that play a major role in the stabilization of metal oxide nanoparticles, and even influence their crystalline structure (e.g. Wang, et al., 2013). Thus, the interface is both structurally and dynamically distinct from either the bulk water or the bulk solid, and exhibits its own unique and important physico-chemical properties that profoundly influence environmental and industrial processes.

Acknowledgement

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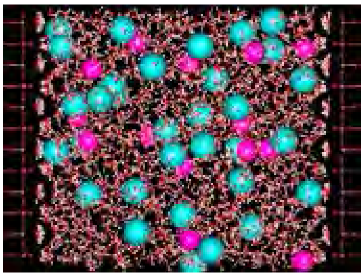

Figure 1 Experimentally-validated classical molecular dynamics snapshot of the structure of aqueous SrCl2 at the rutile (110) crystal surface.

Dr. David J. Wesolowski is a Distinguished R&D Staff Member, Leader of the Geochemistry and Interfacial Sciences Group, and Director of the Fluid Interface Reactions, Structures and Transport (FIRST) Center at Oak Ridge National Laboratory (Oak Ridge, USA). His research interests include: structure and dynamics of interfacial fluids, kinetics and equilibria of ion adsorption at mineral surfaces, equilibrium thermodynamics of fluid speciation and mineral solubilities, heterogeneous reaction kinetics, and electrode/electrolyte interactions in nanoporous materials for electrical energy storage and electrocatalysis. He obtained his Ph.D. in Geochemistry and Mineralogy from the Pennsylvania State University in 1984 (Pennsylvania, USA).

ORAL PRESENTATIONS MONDAY

Reversible trapping of water contaminants on nanoporous carbon electrodes

Mickaël Gineys[1*], **Sandrine Delpeux - Ouldriane**[1], **Nathalie Cohaut**[1]**and François Béguin**[1]

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During the last decade, thanks to the improvement of analytical techniques, a wide variety of micropollutants, like reproductive hormones and pharmaceuticals, have been detected at trace concentrations in wastewater effluents [1-3].

Activated carbons, presently used in tertiary water treatment, appear as the most prevailing and competing adsorbents for the elimination of pollutants, particularly at low concentration. Indeed, their textural properties (high surface area ~ 2000 m^2/g) and the presence of an accessible porous network, allow high adsorption rates to be achieved, reaching nearly 100 %, without generation of by–products. However, the major encountered disadvantage of these materials is their short lifetime due to the regeneration difficulties and expensive processes. Indeed, the high energy consuming conventional methods, essentially based on thermal and chemical treatments, show limited regeneration efficiency. An interesting alternative consists in the polarization of a carbon electrode with the aim to in - situ regenerate the activated carbon loaded by the organic pollutants [3-6].

This study is focused on target pollutant representing different families of micropollutants (solvent, pesticide, hormone, endocrine disruptor, analgesic, anti – inflammatory, antibiotic, neuroleptic …). The adsorption properties and regeneration efficiency have been investigated on selected pollutants, using two activated carbon cloths (ACC) with different nanotextural and chemical properties. The reversible electrochemical desorption was performed through a cathodic or anodic polarization of the adsorbent depending on the selected pollutant adsorbed. Effects of electrochemical parameters as current polarization, electrolyte composition, concentration and electrode potential on regeneration efficiency have been explored. HPLC analysis permits us at the same time to follow the pollutant concentration, to quantify precisely the desorption rates and to observe the stability of targeted pollutant in electrolytic solution under polarization. To complete this study, the textural properties of carbon adsorbent after adsorption and desorption have been investigated with the aim to evaluate the proportion of regenerated porosity. Furthermore the behavior of activated carbon under cathodic polarization has been studied through chemicals and textural characterization techniques.

This type of process should allow the energetic and environmental drawbacks of conventional regeneration methods to be overcome. Such a technique offers great potentialities for the development of soft and controlled in-situ regeneration processes.

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Adsorption kinetics and isotherms of micropollutants onto activated carbon fabric and felt

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A lot of studies have revealed that some organic molecules such as pharmaceutical molecules, solvents, pesticides, etc. are frequently found in water even after treatment at the exhaust of wastewater treatment plants. One of the possibilities for removing these so-called micropollutants is the adsorption on activated carbons. Thus the aim of this work is to better understand the adsorption mechanism of some micropollutants onto activated carbons (ACs) in felt or fabric form.

Eight micropollutants molecules were studied, such as some pharmaceuticals: Carbamazepine (CBZ), Diclofenac (DFN), Ibuprofen (IBP), and Ofloxacin (OFX); an endocrine disruptor: Bisphenol A (BPA), an herbicide: Mecoprop (MCP), a pesticide: Pentachlorophenol (PCP), and a corrosion inhibitor: Benzotriazole (BTA). Adsorption of Caffeine (CAF) which is an anthropic indicator of pollution in waste water was also studied. The ACs (KIP1200 fabric and CSV4 felt, from Dacarb, France) were characterized by N_2 adsorption-desorption at 77 K and CO_2 adsorption at 273 K, pH_{pzc} (point of zero charge) measurements and acido-basic titrations (Boehm method). The adsorption kinetics (at C_0=100 ppm) and isotherms of each adsorbate were studied at pH 7.4 in Na_2HPO_4/KH_2PO4 buffered solutions (about 0.04 mol L-1) using UV spectrometry and HPLC for the analysis of organic molecules in the remaining solution. The kinetics of the single molecule (at $C_0=10^{-4}$ mol L-1) and a mixture of the nine molecules (For each absorbate: $C0=1.1\times10^{-5}$ mol L-1) were also studied. From the network of the adsorption isotherms at 13, 25 and 40°C, the thermodynamic parameters (isoteric enthalpies, entropies, and Gibbs free energies) were determined. The pore size distributions of the carbons loaded with micropollutants were determined by DFT simulation from gas adsorption isotherms, in order to investigate the porosity accessible to the adsorbate.

The activated carbon materials were found to be microporous and mainly ultramicroporous with high specific areas (1560 m²/g for the fabric and 1230 m²/g for the felt). Both contained low amounts of oxygenated surface groups. The pH_{pzc} of the carbon surface were found to be slightly basic (8.75 for the fabric and 7.85 for the felt), indicating positive surfaces at the studied pH.

Kinetics for shorter time were better simulated by diffusion model (t<400 min) and by pseudo second model order for longer time. Equilibrium times (Figure 1) were found to depend on the molecule type following this trend: BTA<CAF<IBP<BPA<MCP<CBZ<PCP<DFN<OFX.

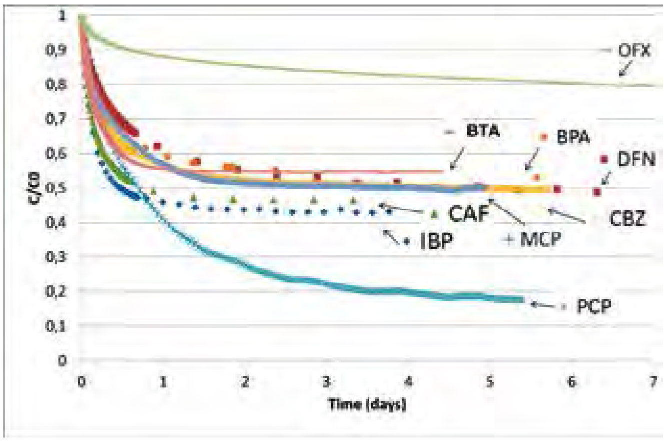

Figure 1 Adsorptio kinetics of each micropollutant on KIP1200 AC (C0=100 ppm, m=16 mg, V=100 mL).

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The shortest ones were observed for the smaller size molecules such as BTA, CAF, IBP and BPA. The longest ones were observed for DFN and OFX and PCP (few days). The diffusion in the porous network measured from kinetics was found to be correlated to the volume and size of the molecules except for PCP. However, the diffusion was also controlled by the affinity between molecules and carbon.

All the adsorption isotherms were better simulated by Langmuir-Freundlich models except for OFX micropollutant for which the best model is the Langmuir one. For the most part of micropollutants, the affinity can be explained by pi-pi interactions as the Langmuir-Freundlich coefficients were found almost proportional to the number of unsaturated electrons in the adsorbates both for fabric or felt.

The comparison of the loaded pollutant volume (calculated from the adsorption uptake and the computed adsorbate volume) with the accessible pore volume (from the pore size distribution of raw ACs) and with the pore volume of the loaded ACs, enabled to predict the sites of adsorption of the micropollutants. We concluded that all the studied molecules would be adsorbed in the ultramicropores and that IBP, CBZ, BPA, CAF and OFX might be located in the supermicropores.

The thermodynamic analysis yielded to values of ΔG°_{298K} typical of a physisorption. Whatever the micropollutants and the adsorbent, the heats of adsorption were found endothermic at low uptake (q_e=0.1 mmol/g) suggesting an interaction of the solvent with the micropollutants prior to adsorption. The increase in the positive entropy variation as decreasing the uptake was observed whatever the micropollutants, suggesting the release of the solvent during the adsorption process at low uptake. As the uptake increased from 0.1 to 1 mmol/g, the enthalpy variations values became more exothermic, suggesting different adsorption sites as a function of the loading rate. The highest exothermicities at saturation were also related to a negative variation of the entropies signifying an increase in ordering observed for adsorption of IBP, MCP and CAF on fabric.

Electrochemical reduction of haloacetic acids in a three-dimensional electrochemical reactor with Pd-GAC particles as fixed filler and Pd-modified carbon paper as cathode

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Haloacetic acids (HAAs) are important disinfection byproducts in chlorinated water. Electrochemical reduction is found to be the efficient and friendly method for the removal of HAAs. Herein, the reductive removal of haloacetic acids (HAAs) in a three-dimensional electrochemical continuous reactor with Pd-granular activated carbon (Pd-GAC) particles as fixed filler and Pd-modified carbon paper (Pd-C) as cathode was studied in this research. Pd-C electrode was prepared from $PdCl_2$ via electrodeposition onto carbon paper; Pd-GAC particles were prepared by the impregnation of Pd^{2+} ions onto GAC [1]. Efficient electrocatalytic reduction of HAAs in this reactor was exhibited. Effects of current density, initial HHAs concentration, and hydraulic retention time on the HHAs removal were investigated.

Under the current density of 0.3 mA/cm^2, HAAs with initial concentration of 120 µg/L were reduced to be less than 60 µg/L with hydraulic retention time of 20 min. Electron transfer and HAAs diffusion both played an important role in controlling the electro-reduction process under the conditions of current density less than 0.6 mA/cm^2 with an initial HAAs concentration ranging from 120 to 600 µg/L (Fig. 1). However, the HAAs diffusion became the primary rate-limiting step when the current density was higher than 0.6 mA/cm^2. The Pd^0 and Pd^{2+} species were detected by X-ray photoelectron spectroscopy [2]. The stability of the electrochemical reactor in the reduction removal of HAAs was also exhibited.

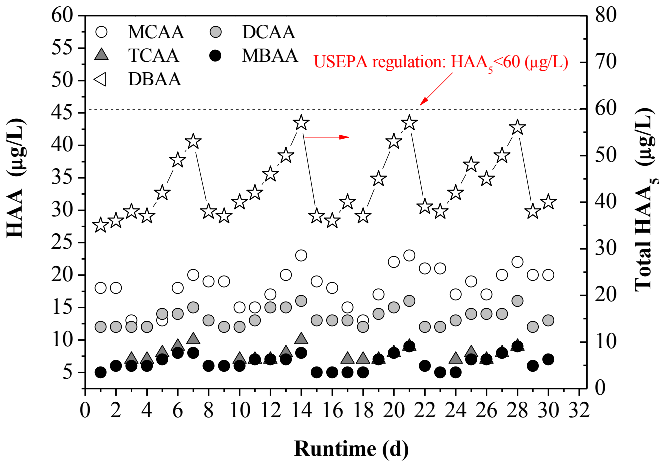

Figure 1 HAAs concentration in the effluent of continuous running (initial HAAs concentration: 120 µg/L; current density: 0.3 mA/cm^2)

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Developing Efficient Polycation-Clay Sorbents for the Removal of Pharmaceuticals and Dissolved Organic Matter

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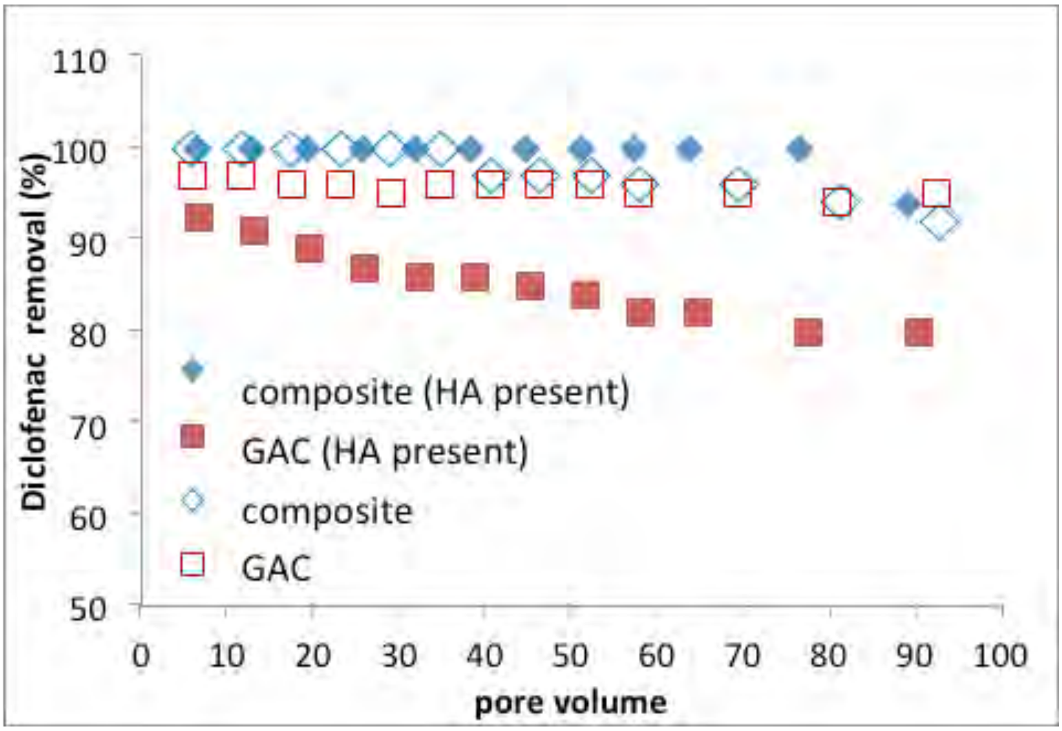
Diclofenac, an anti-inflammatory drug, is one of the most frequently detected pharmaceuticals in water bodies since its removal by most conventional wastewater treatment plants is low. Recently, we have developed an efficient sorbent for diclofenac removal based on the adsorption of a specially synthesized polycation, poly N-methyl 4-vinyl pyridine iodide co styrene (QPVPcS), to montmorillonite. Zeta potential of the clay (-20 mV) decreased (less negative) with an increase in polymer loading and charge reversal (+80 mV) was reached at high polymer loadings (0.2 g/g). This positive charge of the composites promotes electrostatic interaction with anionic diclofenac (pKa=4.15). In addition to electrostatic interactions the polycation has aromatic groups which may induce π–π interaction with the pollutant. To estimate the contribution of these interaction, diclofenac removal (1 mg/L) by a QPVPcS-clay composite and by a polycation-clay composite (no aromatic groups), was studied at various ionic strengths (0-100 mM NaCl). Both composites exhibited complete diclofenac removal at low ionic strength but at higher ionic strengths its removal by the other composite decreased substantially while its removal by the QPVPcS composite was slightly compromised. Hence, we suggest that the π–π interaction have a dominant contribution to diclofenac removal. Electrostatic and π–π interaction can also explain the extremely high affinity of humic acid to the composite. Surprisingly, the presence of humic acid did not compromise diclofenac removal but rather increased it suggesting a synergistic effect. The adsorption kinetics of diclofenac and of humic acid to the composite was substantially faster than to granular active carbon (GAC). The efficiency of diclofenac filtration by GAC and QPVPcS filtration columns in the presence of humic acid and without HA was studied. Diclofenac removal by the composite filter was slightly higher than by GAC. The removal of humic acid was significantly higher by the composite filter. In the presence of HA diclofenac removal by the composite enhanced while its removal by the GAC column was compromised (Figure 1). To conclude, the removal of diclofenc or of humic acid is more efficient by the developed polymer-clay composite than by GAC filters. This advantage is more pronounce in a complex system of simultaneous removal.



Mineralogical investigations of precipitates obtained by treatment of Cu-rich waste water by Ferrite process

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Industry wastewater containing heavy metals is generated in various production processes of metalworking (e.g. electroplating). A commonly used removal process is the precipitation of copper as hydroxide. Another method is the ferrite process: This method involves the addition of Fe^{2+} ions into the solution at an elevated temperature. Subsequent alkalinisation and oxidation of the solution causes the formation of dark brown or black precipitates. Aim of this study was to test the feasibility of the ferrite process for Cu-rich solutions (up to 10 g/L Cu^{2+}) and to characterize the precipitated material. Various experimental conditions were performed. The influence of ageing on the precipitates was investigated too.

The results indicate that this process is an effective and economic method to remove copper. After treatment the concentration dropped down to < 0.2 mg/L. Fresh and aged samples were investigated by X-ray diffraction (XRD). In the fresh sample cuprite (Cu_2O) and goethite (α-FeOOH) were identified. After one hour of ageing, the pattern changed significantly and shows the presence of a cubic structure as the most dominant phase. The decrease of the cuprite reflexes suggests that all copper is incorporated in the ferrite structure. The patterns obtained for the samples with longer ageing time are very similar.

FTIR spectroscopy confirms the results from the XRD analysis. In addition it enables the detection of X-ray amorphous phases. The spectra of the fresh sample show the massive presence of green rust 2 (GR2), a Fe^{2+}-Fe^{3+} layered double hydroxyl-sulphate. Within one hour the GR2 bands decrease strongly. After two days of ageing the GR2 bands disappear, whereas the magnetite bands increase.

Magnetic measurements were performed to determine the Cu-content in the ferrite solid solutions. The measured Curie temperature, however, corresponds exactly to that of pure magnetite, which is about 580°C.

SEM images of the samples show platy crystals with 20 – 80 nm size and ≈ 5 nm thickness and hence confirm the formation of GR2 in the fresh samples. Crystals with octahedral shapes and 5 – 50 nm size were observed as a minor phase. After one hour of ageing GR2 was almost completely transformed in granular crystals < 20 nm size. At the same time, the quantity of idiomorphic octahedral magnetite crystals increased. After twenty days the major phase was magnetite with a size of 20 - 80 nm. TEM bright field images showed that many of the nanocrystals contain characteristic dark cores. Investigations revealed that they are caused by copper in the metallic state. Furthermore, the results show clearly that iron is restricted to the prevalent ferrite phase.

In summary, it can be stated that the ferrite process is a simple and inexpensive method to remove Cu^{2+} ions from wastewaters. The results obtained in this study show clearly, that the postulated formation of copperferrite by ferrite process cannot be confirmed: They point out that almost no Cu^{2+} is incorporated into the ferrite structure. The systematic analysis of the fresh and aged samples shows GR2 as precursor for magnetite. Note that the size of all precipitated phases is less than 100 nm. Depending on reaction condition Cu occurs as oxide like cuprite or tenorite. But GR2 may also effect the reduction of Cu^{2+} to metallic copper. It occurs as agglomerates of only few nanometer large particles or it is enclosed by pure magnetite.

Cross-coupling oxidation of bisphenol A during electro-enzymatic oxidative process

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Bisphenol A (BPA) is catalyzed in an electro-enzymatic reactor by a horseradish peroxidase cathode with the presence of humic acid (HA). During the processes of electrogenerating H_2O_2 coupling HRP-drived oxidative polymerization on the enzymatic cathode, the removal of BPA can achieve 100% within 5 min reaction (Fig. 1). In initial stage of electro-enzymatic reaction (0-3min), the presence of HA inhibits the removal rate of BPA, due to competition between BPA self-polymerization and HA self-coupling reaction. However, in later stage (3-5min), HA significantly promotes the removal of BPA. Results indicate that BPA is oxidized into self-polymers, and then BPA self-polymers decrease and disappear. Furthermore, HPSEC results (Fig. 2) show molecular weight of (HA+BPA) products (6271.4 Da) are much higher than HA self-coupling products (3267.2 Da) and initial HA (1583.8 Da). Therefore, the BPA self-polymers may be incorporated into HA matrix, and HA promotes BPA self-polymerization to cross-coupling reaction.

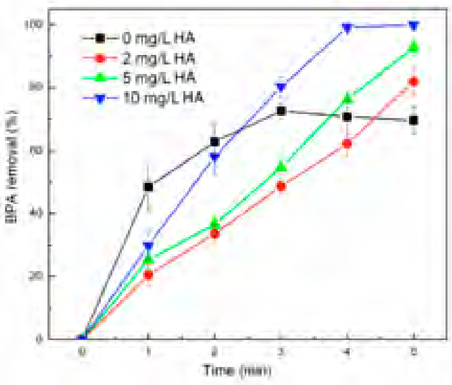

Figure 1 Effect of HA on BPA removal (immobilized HRP amount=25 U, I=5 mA).

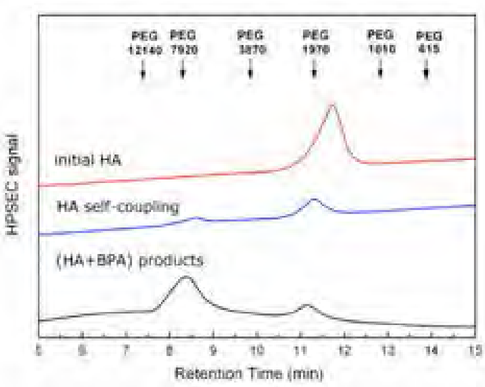

Figure 2 HPSEC chromatograms of products in electro-enzymatic systems. (HRP=25 U, I=15 mA, [BPA]=100 mg/L, [HA]=100 mg/L), 30 min reaction, (i) HA control, (ii) only HA reaction, (iii) both BPA and HA.

Interactions of organic dyes with layered double hydroxides

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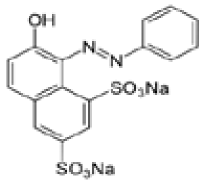
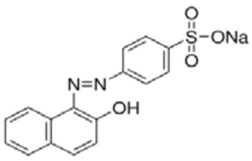
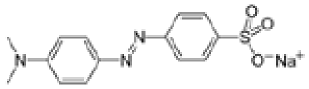
Layered double hydroxides (LDHs)[1] are promising materials for remediation uses due to their lamellar structure and high exchange capacities. In the literature LDHs are presented as effective adsorbents for various types of pollutants. Nevertheless, only a limited number of studies report the influence of common anions on the sorption of toxic anions and the influence of the competitive interactions [2]. In this work, synthetic Mg-Al LDHs ($([Mg^{2+}_{1-x}Al^{3+}_{x}(OH)_2]^{x+}[NO_3^{-}{}_{x/n} \bullet mH_2O]^{x-})$) with NO_3^- as an interlayer and exchangeable anion, were used as adsorbent material. Different characterisation methods were used to investigate the adsorption mechanisms including UV-Vis Spectroscopy, Ionic HPLC and Isothermal Titration Calorimetry ITC. Adsorption mechanisms (kinetics and capacity) were assessed for three various organic pollutants, Methyl Orange, Orange G and Orange II.



Orange G (OG),



Orange II (OII),



Methyl Orange (MO)

The trend in the maximum amount adsorbed was the following MO>>OII≈OG. All ionic species were analyzed (including Na^+ as dye counter-ions), in order to elucidate the adsorption mechanism. Sorption tests were also performed in the presence of such competiting species as common ions (SO_4^{2-}) or heavy metal pollutant (Chromium). Nanocalorimetry measurements allowed the thermal effects of the complexation process to be quantified. The sorption phenomenon was observed to be exothermic in all cases, with the intensities being a function of the dye structure.

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Study photocatalytic reactions for pollution remediation by electron ionisation mass spectrometry

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Since the industrial revolution, an increasing global population demands more resources and energy and it has led to a greater awareness of pollution and air quality. Photocatalysts can be an effective tool against greenhouse gases, promoting reactions under a certain light wavelength. This research describes a novel methodology for the real time in-situ study of solid-gas phase photo-catalytic reactions using different LED that irradiates in the UV. Photo-catalytic samples consisting of pressed pellets of rutile and anatase crystalline forms of TiO_2 and commercially available photoreactive tile. An ultra-high vacuum right angled bleed valve allowed a controlled flow of gas from the main reaction chamber at atmospheric pressure to a mass spectrometer operating at a vacuum of 10^{-5} mbar. The apparatus and methodology have been demonstrated to provide high sensitivity (ppb). The rate of degradation of NO_2 attributed to a photo-catalytic reaction at the TiO_2 surface was sensitive to both crystal structures (anatase or rutile) and wavelength of irradiation.

Keynote

Applications of electrosorption systems for waste water recovery

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Electrosorption Technology has been developed in dealing with the water shortage problem of the world. It has been found that the electrosorption technology is suitable for the desalination treatment of difficult waters such as waste water and mine water, due to its robust nature and low energy as well as chemicals consumptions. Several large scale industrial applications of electrosorption technology were investigated in this presentation. Various waste waters from chemical plant, steel mill, petrol refinery and coal mines as well as municipal sewage plant were treated with electrosorption technology and regenerated as fresh water supplies for corresponding industries, at capacities of 0.6 to 3.5 million gallons per day. Satisfactory continuous operations have been achieved for duration of 2 to 5 years with relatively lower power consumption and zero chemicals consumption. Studies on the real operations and laboratory experiment have shown that the deionization effectiveness of electrosorption technology is determined greatly by electrode material properties and surface oxidation status as well as cell configurations.

Keynote

Continuous performance of double-layer technologies for water desalination and energy harvesting using flow electrodes

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Capacitive technologies, such as capacitive deionization[1] and energy harvesting based on mixing energy ("capmix" and "CO_2 energy"),[2] are characterized by intermittent operation: phases of ion electrosorption from the water are followed by system regeneration. From a system application point of view, continuous operation has many advantages, to optimize performance, to simplify system operation, and ultimately to lower costs. In our study, we investigate as a step towards second generation capacitive technologies the potential of continuous operation of capacitive deionization and energy harvesting devices, enabled by carbon flow electrodes using a slurry based on conventional activated carbon powders.[3] We show how the water residence time and mass loading of carbon in the slurry influence system performance. The efficiency and kinetics of the continuous salt removal process can be improved significantly by optimizing device operation, without using less common or highly elaborate novel materials. We demonstrate, for the first time, continuous energy generation via capacitive mixing technology using differences in water salinity, and differences in gas phase CO_2 concentration. Using a novel design of cylindrical ion exchange membranes serving as flow channel, we establish the ability to continuously extract energy from available concentration differences that otherwise would remain unused. These results may significantly contribute to establishing a sustainable energy strategy when implementing energy extracting for sources such as CO_2-emissions from power plants based on fossil fuels.

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Keynote
Capacitive deionization based on flowable electrodes

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Koki Urita[2,4], **Theodore Tzedakis**[3], **Fabien Chauvet**[3], **Pierre-Louis Taberna**[2],
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Recently, suspension electrodes ('flowing electrodes') have emerged as a mode for achieving high capacity and scalable systems for a range of infrastructure-level challenges (Fig 1a). The core idea behind flowing electrodes is that the active material (e.g. carbon) can adsorb ions *and transport/store electrons* to and from electrodes via percolation networks (Fig 1b). Thus, the physical attributes of these percolation network plays a large role in the performance of these systems (desalination/energy storage/generation/electrolysis). Furthermore, the dynamic nature of pumping a suspension in order to charge (adsorb ions) or discharge (desorb ions) charged particles is the defining difference between suspension electrodes and film electrodes. The physical make-up of the composite suspension electrodes, in terms of weight %, active material size and shape, and rheological principles are critical in order to understand the performance of a suspension electrode system.

In this talk we highlight the material science aspects of suspension-type electrodes that make it possible to eke the best possible combination of electrochemical properties in terms of long term cyclability and electrosorption capacity. Furthermore, capacitive suspension electrodes are introduced as a mode for removing ions from sea or brackish waters. We describe several key aspects toward the design and function of capacitive suspension electrodes in terms of enhancing the rheological, electrochemical, and kinetic aspects of these composite-type electrodes.

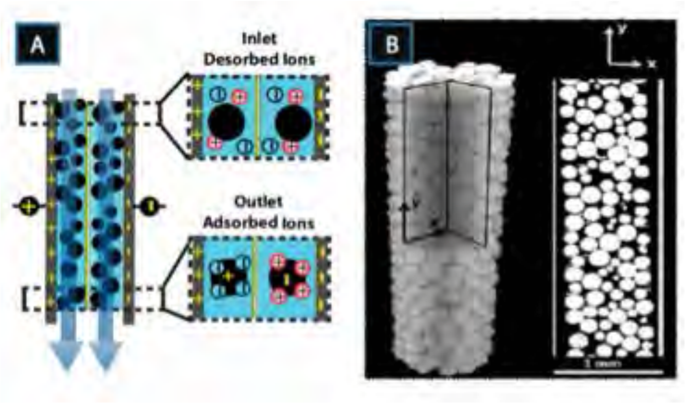

Figure 1 (a) Flowing electrode (adsorption occurs at the outlet), and XCT of percolation networks of contact points between carbon active materials.

Keynote

Water desalination by capacitive deionization - Advantages and limitations

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Capacitive deionization may serve as energy efficient method for salt removal from brackish water (<5000ppm). However, capacitive deionization may have advantages over other competitive desalination methods. One advantage introduced here is what we call “selective desalination”. Since the salt is electro-adsorbed onto activated porous carbon electrode, the pores could be designed by applying a CVD process to be in a shape which doubly charged ions like magnesium and calcium ions, which are important nutrients, could not be electro-adsorbed while sodium ions could be removed selectively from aqueous solutions. In this way we can retain the magnesium and calcium ions in the feed desalinated water. Another advantage is the possibility to remove boron from water in one stage by exploiting the pH changes which occur nearby the negatively charges electrode due to surface reactions or water reduction at the cathode side, in order to transfer boric acid (which is the dominant form of boron contamination in water at neutral pH) into borate ion which could be electro-adsorbed onto the positively polarized electrode.

We also addressed one of the main limitations of the capacitive ionization method which we call herein the “Rocking Chair” problem. We are able to calculate the amount of cation and anion adsorbed/desorbed onto/from the high surface area carbon fiber electrodes as a function of the potential difference applied. It was revealed that the amount of counter-ions and co-ions electro-adsorbed onto the activated carbon electrodes are equal from both sides of the PZC at potentials in the range of about 150mV. As a consequence, it was recommended to work at narrow potential domains , i.e. the capacitive deionization cell should not be completely discharged to 0 volt, but rather to higher potentials (subject for optimization). By this approach, we were able to demonstrate high charge efficiencies in CDI based desalination processes but on the account of the salt removal capacities per charge-discharge cycle.

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Keynote

Free Radicals Generating from Catalytic Decomposition of H_2O_2: New Strategies and Applications

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The increasing worldwide contamination of fresh water systems with various toxic chemicals is becoming the crucial environmental problem facing humanity [1]. The heterogeneous Fenton process has long been regarded as a promising alternative for the remediation of refractory compounds in aqueous solution [2]. However, the poor stability and low efficiency of solid Fenton catalysts hamper the process from large-scale application. Two strategies have been implemented in the development of solid Fenton-like catalysts: (1) Supported gold catalysts have proved to outperform the iron-based Fenton catalyst due to its high stability for the degradation of phenol (Figure 1-2) [3-5]; (2) Redesign Fe-based solid catalysts by improving the catalytic efficiency in H_2O_2 decomposition to create OH radicals (Figure 3).

Our studies are mainly focusing on the development of solid Fenton-like catalyst using different preparation methods and raw materials. In particular, the structures of nanoparticles were characterized. By evaluating the catalytic performance, the kinetics of degradation of persistent organic compounds was carried out. The structure-performance of those catalysts were established on the basis of characterization results.

In summary, Au/carbon has proved to be effective Au-Fenton catalysts for the degradation of BPA by the production of OH·. It showed high activity and durability in a broad pH range (3.0-7.0). We tentatively attribute the generation of ·OH to two factors: (1) Au atoms are polarized or negatively charged on the carbon surface, which is abundant of dangling bonds; (2) there is few complete basel sites or other sites to scavenge ·OH. In addition, the unique structural configuration of iron atoms and the reducible electronic properties of FeOCl are responsible for the excellent activity of Fenton reaction. The high productivity of OH· in this system makes solid Fenton process more practical application for water treatment.

We believe the reported solid Fenton-like system can be an excellent alternatives for rapid purifying drinking water, which may be contaminated with toxic and undegradable organic compounds. Our work can inspire further study regarding degradation of toxic organic compounds using this simply and stable solid Fenton system without extra energy input such as photon and electricity.

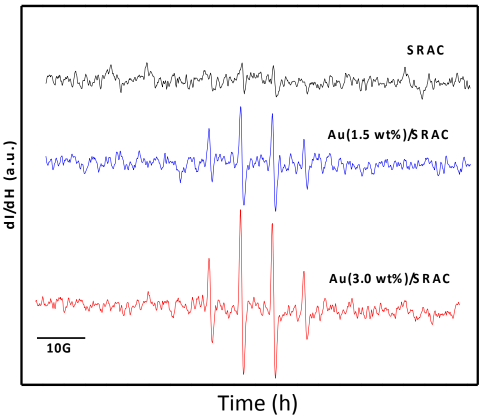

Figure 1 Time-dependent BPA degradation over Au/Carbon catalysts with different Au loading amount

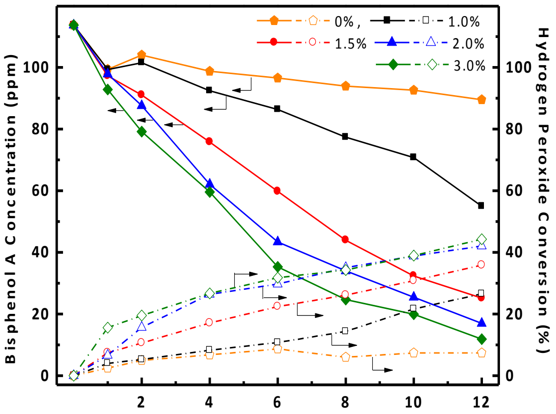

Figure 2 DMPO- trapped EPR spetra of Au/carbon with different Au loading amount

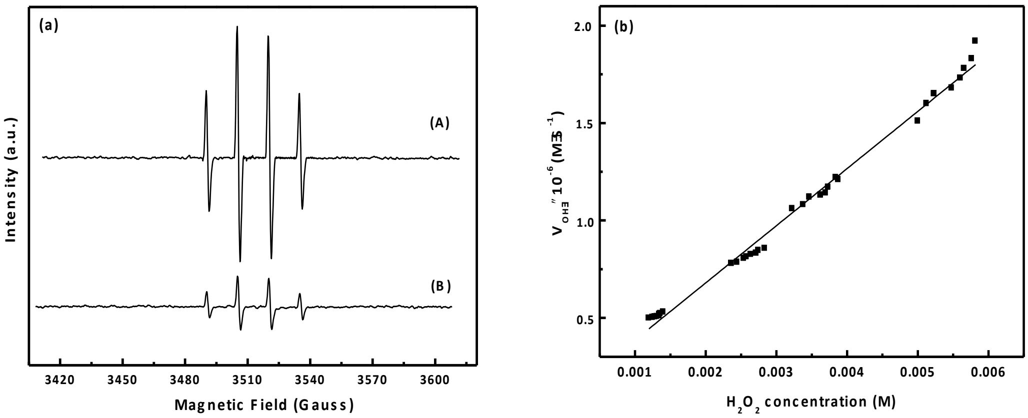

Figure 3. (a) DMPO trapped electron paramagnetic resonance spectra (EPR) at 120 s over FeOCl (A) and conventional Fenton reagent, Fe^{2+}(B); (b) Formation rates of OH· as a function of H_2O_2 concentration over FeOCl.

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Fast degradation in immobilized photocatalytic microreactors

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Photocatalytic reactors form an interesting platform for environmental and chemical applications. Despite the attractive features of photocatalysis, true implementation remains limited. Fundamental understanding of the processes should include mass transport, light distribution and true reaction kinetics. Here we present a microreactor platform incorporating an immobilized photocatalytic layer in which mass transport and light distribution are accurately desribed. Experimental observations indicate very fast degradation kinetics for a variety of compounds, that are orders of magnitude faster compared to generally reported. The microreactor is modeled by implementing a flux boundary condition into the convection diffusion equation [1]. The flux boundary condition describes the complete mass transport, light distribution, and reaction inside the porous catalyst film. This approach is crucial as it allows one to obtain true reaction kinetics, instead of overall or apparent conversion kinetics. Only with true kinetics it will be possible to compare catalysts accurately. As such, a Thiele modulus can be defined that includes the light adsorption characteristics and an internal effectiveness factor is presented that elucidates the relative limitations of mass and light transport within the photocatalyst layer.

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Fast inhibition of direct ammonia oxidation on thermally decomposed iridium oxide films through a change in local pH

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Electrochemical oxidation has gained high attention recently as an efficient method for ammonia removal from polluted waters. In this study, we tested anodes with thermally decomposed iridium oxide films (TDIROF), which were shown to oxidize free ammonia (NH_3) via a direct electron transfer to molecular nitrogen (N_2) and nitrate (NO_3-). Unfortunately, TDIROF anodes are rapidly deactivated during ammonia oxidation which has commonly been attributed to surface poisoning by adsorbed elemental nitrogen (N_{ads}).
In this study, we showed that the fast deactivation of TDIROF not necessarily has to result from surface poisoning. Instead, we propose that ammonia oxidation and oxygen evolution lead to a pH drop close to the anode surface resulting in a low availability of the actual reactant, NH_3, in the vicinity of the electrode. In cyclic voltammetry (CV) experiments we showed that TDIROF deactivation can be compensated or even overcompensated by polarizing the electrode into the hydrogen evolution region (HER) (Figure 1). The ammonia oxidation peaks of the scans 2 to 5 (A1 solid red line) are higher than the peak in the first scan (A1 dashed black line). The difference results from the fact that in the scans 2 to 5 the CV has been extended far into the HER compared to the first scan starting from open circuit potential (OCP). We propose that hydrogen evolution consumes protons and raises the local pH at the potentials in the HER thereby increasing the amount of NH_3 locally. This effect is stronger the longer the potential remains in the HER and thus depends on the lower return potential ($E_{lower\ return}$) (inset Figure 2). Other CV experiments showed that TDIROF activity for ammonia oxidation could be recovered by letting the electrode rest at OCP for some time before the next anodic scan. The rest time allowed to balance out the pH value in the Nernst diffusion layer and the bulk solution, so that the ammonia oxidation peaks for each scan are equal. If TDIROF deactivation would result from surface poisoning by Nads a rest time at OCP would not be sufficient to reactivate the electrodes. Potentiostatic bulk electrolysis experiments showed that direct ammonia oxidation at TDIROF continued steadily for 35 hours (Figure 2). If the electrode surface was poisoned one would expect that the process slows down or stops completely. We conclude that the fast deactivation of TDIROF is mainly caused by a diffusive inhibition which can be reduced in hydraulically optimized cells. The inhibition mechanism we propose can be generalized for all electrode materials since acidic conditions prevail in the Nernst diffusion layer of any anode.

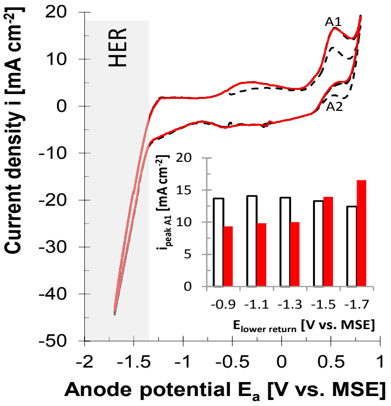

Figure 1 Five consecutive cyclic voltammograms (CV) recorded in 0.5 M Na_2SO_4 + 0.125 M $(NH_4)_2SO4$ on TDIROF. Scan rate: 200 mV s-1, pH = 9.25. Inset: Current density peak A1 of the 1st (empty bar) and 5th scans (solid bar) in CV with changing lower return potential.

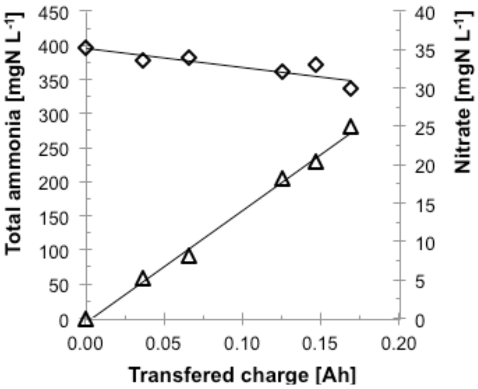

Figure 2 Total ammonia and nitrate concentrations with respect to transferred charge during potentiostatic electrolysis of 0.015 M $(NH_4)_2SO_4$ + 0.11 M Na_2SO_4 + NaOH. Anode potential: 0.6 V vs. MSE.

Keynote

Carbon Nanofiber and Graphene Composites made by Electrospinning for Capacitive Deionization

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Capacitive deionization technology (CDI) is of great potential as an effective approach to removing salt ions from salted water. One of the challenged issues is the fabrication of high performance electrodes. In this talk, we will report a novel strategy for fabrication of activated carbon nanofiber/reduced graphene oxide (ACF/RGO) composite materials by electrospinning, followed by CO2 activation treatment at 800 oC. The morphology, mechanical property and conductivity of the electrospun ACF/RGO electrode materials were examined, and the NaCl removal capacity of ACF/RGO electrodes was tuned by changing the graphene ratio. The electrospun nanofibers have two functions: a decorating agent for immobilization of graphene and a substrate to prevent the agglomeration of graphene. The incorprated graphene helps to improve the conductivity and the pore size distribution of the ACF/RGO electrodes, evidenced by the results that the ACF/RGO-10 has an electrosorption capacity of 9.2 mg g-1, which is the highest among the ACF/RGO composites fabricated under the conditions.

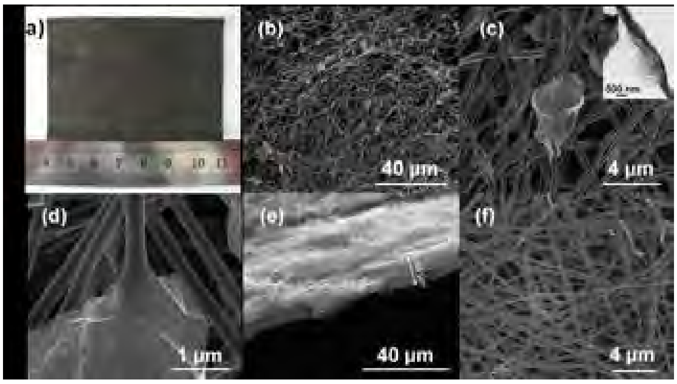

Fig. 1 (a) Photo of ACF/RGO-10, (b)-(d) SEM images of ACF/RGO-10, inset in Fig. 1(c) is the typical TEM image, (e) Side-view SEM image of ACF/RGO-10, and (f) SEM image of ACF

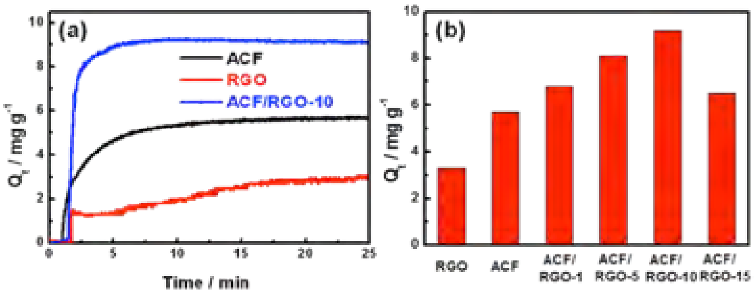

Fig. 2 (a) The NaCl electrosorption capacity of ACF, RGO and ACF/RGO-10 electrodes vs. time in CDI; (b) the desalination capacity of ACF, RGO and ACF/RGO-X (X stands for the weight ratio of RGO in the electrodes), for which the test conditions are Vcell :1.2 V, VNaCl:30 mL, and C0:400 mg L-1

Effect of pore size and its dispersity of porous carbon on capacitive deionization

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Porous carbons continue to dominate the field of capacitive deionization (CDI) for good reasons: it is an abundantly available resource with low or moderate costs yielding a high CDI performance. All electrodes used for CDI are porous at various length levels and even per se non-porous carbons (e.g., carbon nanotubes) show a large pore volume comprised from the space between particles; thus, it is of high importance to consider the total pore volume (inter- and intraparticle porosity) and its impact on the resulting CDI performance. In particular, we will review the importance of porosity measurements, the pitfalls of applying deconvolution algorithms to conventional sorption analysis data, and novel strategies to develop predictive tools for CDI sorption capacities and kinetics.

Recently, studies on microporous carbon gave convincing evidence that pores smaller than 2 nm are of high importance for the electroadsorption capacity of salt in CDI electrodes.[1] This has been a change of paradigm: before, it was believed that rather larger pores, so called mesopores (2-20 nm), are beneficial for CDI capacity.[2] New results by us, employing model carbons with precisely tuned porosity, however, show that micropores contribute to much higher degree to the salt sorption capacity compared to mesopores.[3] We used our novel nanoporous carbons to establish a predictive tool: based on cumulative pore size distributions, we were able to predict at 1.2 V and 5 mM salt concentration the salt electrosorption capacity of a large array of carbon materials in the literature. In a second step we also used a two-dimensional transport model to predict the sorption kinetics and to evaluate the optimum electrode material compaction level for salt electrosorption.

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Preparation of a MnO_2/Carbon Composite Electrode for Electrosorptive Removal of Heavy Metal from Water

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It has been believed that the physical properties and the structure of electrode materials dominate its electrosorptive performance. Manganese dioxide (MnO_2) has been extensively studied as an effective absorbent to remove heavy metals from water. Meanwhile, MnO_2 is a promising electrode material for electrochemical supercapacitors because of its high specific capacitance, good cycle stability, low cost, eco-friendly nature and abound availability. MnO_2/carbon composite materials show great potential as electrodes for electrosorptive removal of contaminant ions from water. Yang et al.[1] synthesised MnO_2/nanoporous carbon composites and successfully used them as electrode in capacitive deionization technology. In addition, MnO_2/carbon materials composite showed great adsorption ability to remove heavy metal ions from waste water [2, 3]. Althrough MnO_2 is an effective absorbent for many metal ions and a promising electrode material for electrochemical supercapacitors, no previous study combines the two properties and uses it as electrode to remove metal ions by electrosorption process.

In the present study, a simple and cost-effective electroplating approach was used to directly deposit a thin MnO_2 layer on the surface of carbon cloth (CC). Morphology, structure, and capacitive properties of the prepared MnO_2/CC electrode were characterized. On the basis of the materials characterization, we evaluated the electrosorptive performance of the MnO_2/CC electrode on Cu^{2+} and Pb^{2+} removal. The scanning electron microscope images clearly showed the film of nano MnO_2 clusters on CC surface. With increasing deposition time, the thickness of nano clusters gradually increased. An XRD pattern for the MnO_2/CC electrode indicated a long-range disorder of MnO_2 in these composites. Electrochemical characteristics of the MnO_2 /CC electrodes prepared for different deposition periods were evaluated by using cyclic voltammetry (CV). The voltammetric current response, and consequently the capacitance of the coating, increased substantially with increase in deposition time from 500s up to 7200s. The capacitance, however, it calculated that deposition time of 1000s was optimum for achieving maximum capacitance and the capacitance was as high as 380 F/g. The MnO_2/CC electrodes showed high efficiency on electrosorptive removal of Cu^{2+} and Pb^{2+} from water. Voltage, pH, and the amount of loading MnO_2 significantly influenced the electrosorption performance in Cu^{2+} and Pb^{2+} removal.

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Zinc oxide nanorods coated carbon electrodes for improved energy efficient capacitive desalination of brackish water

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Capacitive deionization (CDI) with its low energy consumption and capital costs accompanied with a smaller footprint and portability is catching recent attention worldwide, especially for desalting brackish water. It works on the principle of electric field mediated ion adsorption in the electrical double layer (EDL) formed at the electrode surface upon the application of an external potential. Symmetrically assembled activated carbon cloth (ACC) electrodes having a high surface area can increase the ion adsorption capacity, increasing the salt removal efficiency of the system. By coating the ACC surface with a dielectric material like zinc oxide nanorods (ZnO)[1], we were able to increase charge efficiency of the composite electrode by 20%, attributed to increase in capacitance of the electrode. Uniform electric field distribution at the ZnO nanorods surface increased the ion adsorption and desorption rate at the electrode surface, increasing the salt removal efficiency by 45%. Faster ion transfer rates also contributed to reducing the desalination and regeneration times by an average of more than 50%, leading to a net power consumption of less than 25 mW per adsorption cycle. The reduction in regeneration time led to a reduction in the overall water wastage during the process thus improving the recovery rate. The electrodes were characterized for active surface area, capacitance from cyclic voltammetry curves and theoretical assessment of surface area utilization and magnitude of electric field force acting on an ion of unit charge for an applied potential. Some results on larger electrode sized capacitive desalination prototype will also be discussed.

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Geochemical and microbiological characteristics during in situ chemical oxidation and in situ bioremediation at a diesel contaminated site

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While *in situ* chemical oxidation with persulfate has seen wide commercial application, investigations into the impacts on groundwater characteristics, microbial communities and soil structure are limited. To better understand the interactions of persulfate with the subsurface and determine the compatibility with further bioremediation, a pilot scale treatment at a diesel contaminated location was performed consisting of two persulfate injection events followed by a single nutrient amendment. Groundwater parameters measured throughout the 225 day experiment showed a significant decrease in pH and an increase in dissolved diesel and organic carbon within the treatment area. Molecular analysis of the microbial community size (16S rRNA gene) and alkane degradation capacity (*alkB* gene) by qPCR indicated a significant, yet temporary impact. Analysis of soil samples with sequential extraction (Table 1) showed irreversible oxidation of metal sulfides (Figure 1), thereby changing subsurface mineralogy and potentially mobilizing Fe, Cu, Pb, and Zn. Additionally, irreversible changes to soil organic matter quality were measured (Figure 2). Together, these results give insight into persulfate application in terms of temporal and structural effects on soil structure, microbiology, and risks.

Table 1 On-line extraction steps

	Extraction solution	Targeted soil Component
1	0.01 M $CaCl_2$	Reversibly bound cations on clays and organic matter
2	2% H_2O_2	Organic Matter
3	0.45 M HNO_3	Easily extractable sulfides, oxides and carbonates
4	3 M HCl	Amorphous and crystalline Fe and Mn hydroxides, clay minerals, feldspars and pyrite

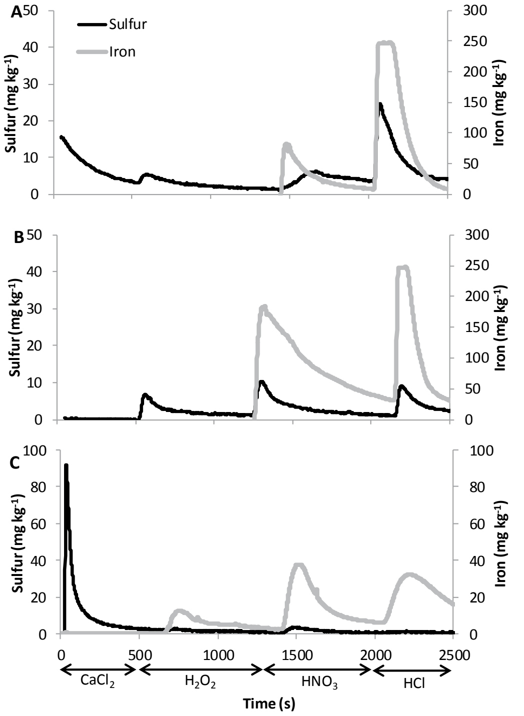

Figure 1 On-line sequential extraction of soil samples from before treatment (A), after the first persulfate injection (B), and at the end of the experiment period (C) for sulfur (black line, left axis) and iron (gray line, right axis).

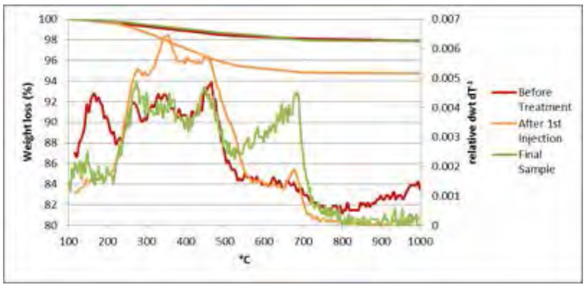

Figure 2 Changes in SOM as measured by TGA analysis. Total weight loss is given on the left axis. On the right axis the derivative of weight loss with respect to temperature relative to the total weight loss is given to allow comparison of the relative contribution of different soil components.

Removal of MTBE from groundwater by adsorption and catalyzed ozonation

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Groundwater contamination with methyl tertiary butyl ether (MTBE, a petrol originated additive) forms a threat to drinking water supply from groundwater, mainly because of its bad taste and odour. Hydrophobic zeolites were shown to be effective for removal of MTBE from water at low concentrations (0-100 µg/L). The zeolite can be regenerated using advanced oxidation processes. By combining adsorption and oxidation, oxidation can take place at elevated concentration levels compared to oxidation in the bulk water phase. A second advantage is the selective adsorption of MTBE excluding natural organic matter from the oxidation. Moreover, catalytic activity of the zeolites may enhance the oxidation process.

In this research the combination of adsorption and ozonation was tested for a high silica ZSM-5 type zeolite. Main objectives are to find optimal conditions for regeneration of zeolite, and to investigate long term performance. This was tested by batch ozonation experiments. Most regeneration experiments were performed with powdered adsorbent and long term performance was investigated with zeolite beads. The zeolite based process was compared with a granular activated carbon (GAC) based process.

Ozonation experiments showed that the zeolite acts as a strong catalyst in the ozonation of MTBE. In presence of activated carbon MTBE was oxidised at lower rate and less ozone was consumed. Addition of hydrogen peroxide resulted in higher ozone consumption without enhancing MTBE ozonation. So radicals formed in the bulk liquid may not be able to reach MTBE adsorbed on zeolite. pH did not have a significant effect on MTBE oxidation. MTBE oxidation increased at a pH of 13, but this pH damaged the zeolite structure. Oxidation rate on zeolite beads was faster than on zeolite powder. At typical groundwater temperature (10°C) MTBE ozonation was faster than at room temperature, due to better solubility of ozone at low temperature.

In long term experiments zeolite and activated carbon were reused for several cycles of MTBE adsorption and ozonation. Zeolite was used for 8 cycles, without observing a negative trend in the oxidation rate (Figure 1) or MTBE adsorption capacity. Decrease in oxidation rate (Figure 1) and MTBE adsorption capacity were observed for GAC within 5 cycles. So GAC is less suitable in combination with ozonation.

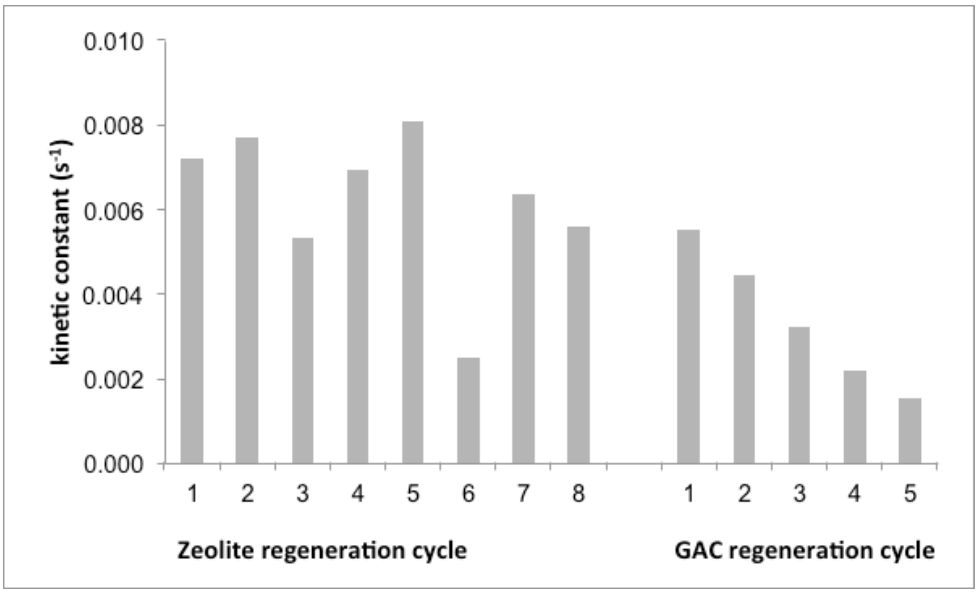

Figure 1 Effect of regeneration cycle on MTBE ozonation rate (presented as kinetic oxidation constants) for zeolite and GAC

An Innovative 2-Stage Process for the Recovery of Phosphorus and Recycling of Ferric from Ferric Sludges Generated in Water and Wastewater Treatment

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ABSTRACT

Ferric salts are used extensively in wastewater treatment to precipitate P, and as coagulant in water treatment. In all cases, large amounts of ferric sludge are produced. The ongoing chemical supply and sludge disposal represent a major operating cost to the water industry. A novel 2-stage process for Fe and P recovery from ferric phosphate sludge has been developed to enable the on-site recycling of ferric for such applications. In Stage I, PO_4 is released in solution after the addition of a sulfide solution to initiate FeS precipitation. In Stage II, FeS is electrochemically oxidised to elemental sulfur that is deposited on the anode and generates a low-pH Fe solution for reuse. Simultaneously the cathodic reduction of sulfur forms sulfide, which can be reused in Stage I to create a fully integrated process (Figure 1).

RESULTS AND CONCLUSIONS

The process has been implemented at lab-scale with several consecutive runs being performed successfully whereby real FeS precipitate formed in Stage I (~3 g Fe/L) is fed to the anode of Stage II and the cathode effluent from Stage II used to form FeS in Stage I. Up to 70% P was recovered in solution in Stage I at pH 4 and 1.5 S:Fe molar ratio. Additionally, up to 83% of the volatile suspended solids (VSS, mainly organics) co-precipitated with the FeS particles. After feeding the FeS-VSS suspension to the anode of Stage II, up to 60% Fe and 50% S were recovered in the anodic and cathodic solutions respectively. The VSS contained in the anodic solution were easily removed by gravity settling. Peak current densities were 9.5 ± 4.2 A m^{-2}, while power requirements were 2.4 ± 0.5 kWh/kg Fe, which offers a significant economic advantage compared to the purchase of ferric chemicals. The demonstration of this process concept is an important stepping-stone towards a full-scale implementation in both drinking water and wastewater industries.

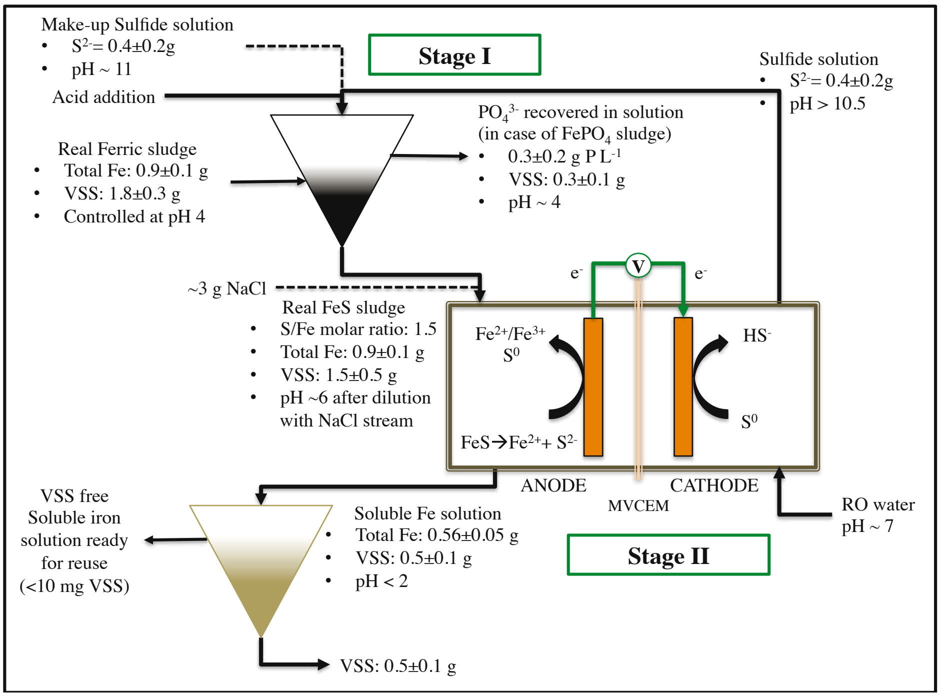

Figure 1 Two-Stage Iron and phosphorus recovery process

Heterogeneous Fenton oxidation of catechol and 4-chlorocatechol catalyzed by nano-magnetite: role of the interface reaction

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The nano-magnetite catalyzed Fenton oxidation of catechol and 4-chlorocatechol in aqueous solution was investigated. The synthesized nano-magnetite (MNPs) was used as catalyst and characterized with various methods. Batch experiments showed that only about 10 % of catechol or 4-chlorocatechol adsorbed onto nano-magnetite, however almost all the parent compound could be removed within 2 h after addition of H_2O_2. The oxidation curves of catechol and 4-chlorocatechol were best fitted by the pseudo-first order and pseudo-third order kinetic model, respectively. The reduce of pH and the analysis of oxidation intermediates and products measured by ion chromatography (IC) and GC/MS suggested the generation of carboxyl acids. The electron spin resonance (ESR) spectroscopy showed that the reactive oxygen species (ROS) were •OH and oxygen-centered radicals in both oxidation systems, and carbon-centered radicals were only detected during the oxidation of catechol. The low iron leaching indicated a heterogeneous reaction mechanism. Moreover, in situ attenuated total reflection FTIR (ATR-FTIR) spectroscopy showed the adsorbed catechol or 4-chlorocatechol remained at the surface during oxidation, implying an Eley-Rideal mechanism. Accordingly, a shematic diagram of oxidation mechanism of catechol or 4-chlorocatechol in the MNPs/H_2O_2 system was proposed.

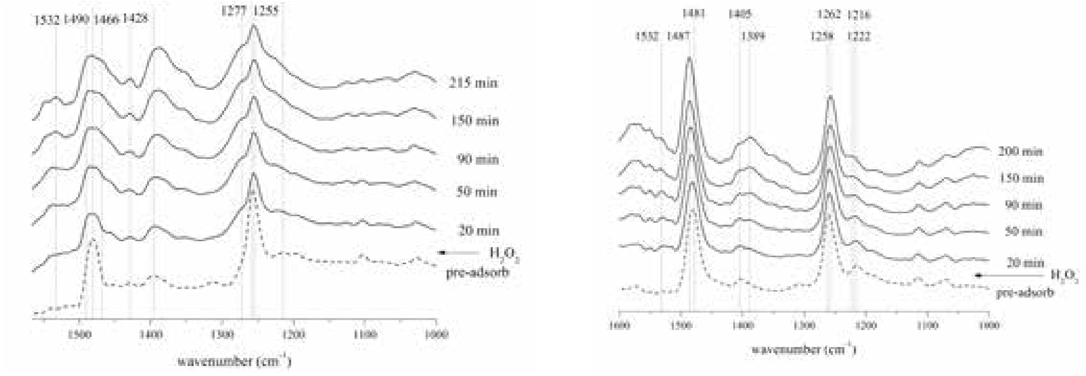

Figure 1 ATR-FTIR spectra of catechol (right) and 4-chlorocatechol (left). $[H_2O_2]_0$= 0.05M; pH=6.5; $[\text{catechol}]_0$=$[\text{4-chlorocatechol}]_0$= 1 mM.

Synthesis and complexation properties of new polyvinyl alcohol (PVA)-based chelating polymers

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A series of water-soluble polyvinyl alcohol (PVA)-based chelating polymers with various proportions of sorption sites were obtained. They were synthesized by reaction between PVA and ethylenediaminetetraacetic acid (EDTA) via Mitsunobu's reaction in order to afford PVA(ETA). Various functionalisation rates were reached (5, 10 and 15% in EDTA) and resulting copolymers were able to be tested for ion selective liquid-liquid extraction. Different characterisation methods were used to investigate complexation properties of PVA(EDTA) including High-Performance Liquid Chromatography (IC for Ionic Chromatography), Isotherm Titration Calorimetry ITC and polarography. Performances of PVA(EDTA)$_{15\%}$ were assessed in presence of several metal cations as Co(II), Ni(II), Pb(II), Zn(II) and Cu(II) in aqueous solution. Selectivity could be established between given metallic cations as function of their affinity towards PVA(EDTA)$_{15\%}$. Moreover, great sorption capacities can be reached in the case of some cations. For example, the maximum sorption quantity for Co(II) is 1.4 mmol.g^{-1} which is comparable to resins commonly used in decontamination process. Nanocalorimetry measurements allowed the knowledge of thermal effects of the complexation process. It is possible to note an exothermic sorption phenomenon in the case of Co(II) (Figure 1).

Sorption tests of these metal cations were investigated in a multi-component solution occurring from industrial effluent based on Ca(II) and Mn(II) ions. Results achieved were similar to that obtained in water. Finally, the modification of different parameters, including EDTA rates and polymer chain lengths, was assessed and complexation tests have allowed us to determine the optimal structure for water decontamination.

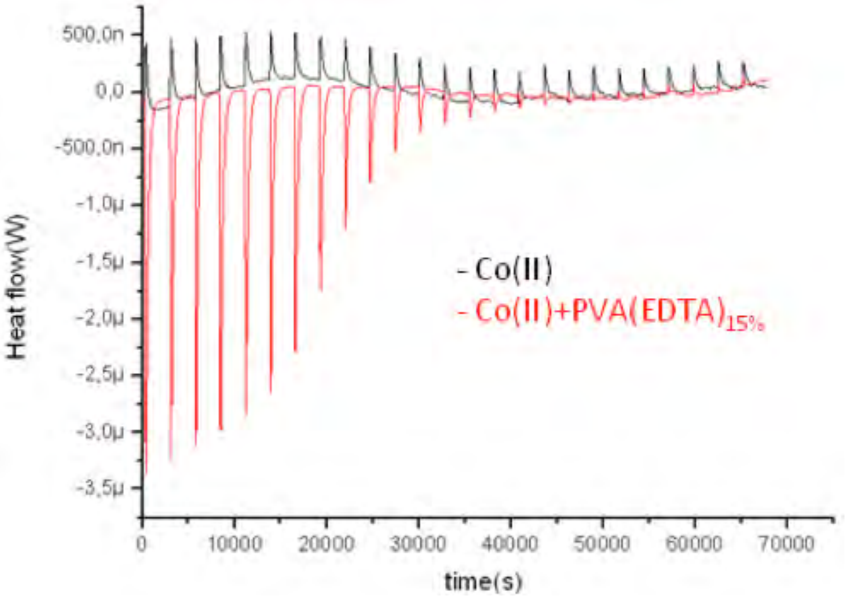

Figure 1 ITC data describing the interactions of Co(II) cations with PVA(EDTA)$_{15\%}$

Sorption tests of these metal cations were investigated in a multi-component solution occurring from industrial effluent based on Ca(II) and Mn(II) ions. Results achieved were similar to that obtained in water. Finally, the modification of different parameters, including EDTA rates and polymer chain lengths, was assessed and complexation tests have allowed us to determine the optimal structure for water decontamination.

Non linear optical tools to study ions remediation processes

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Water pollution has a large impact on the everyday life of people. This topic requires of combining all possible skills to understand better fundamental mechanisms and improve the **remediation processes**. This **multidisciplinary** work at frontier between physical methodology, organic chemistry and physical chemistry of solutions gives a new approach to understand the **mechanisms of depollution** in order to optimize them. Solvent extraction, discussed here, is one of the most common and widely used processes to separate and concentrate substances in solution. The phase transfer reaction occurring at the liquid-liquid interface is often facilitated by the formation of complex species using oil-soluble ligands, also called extractants. These extractants have some slight amphiphilic features and the complexation will affect their interfacial properties. Today, it is considered essential to understand the organization of these extracting molecular compounds at the interface both in absence and during the extraction process in order to get a clear **molecular picture** of the extraction phenomena.

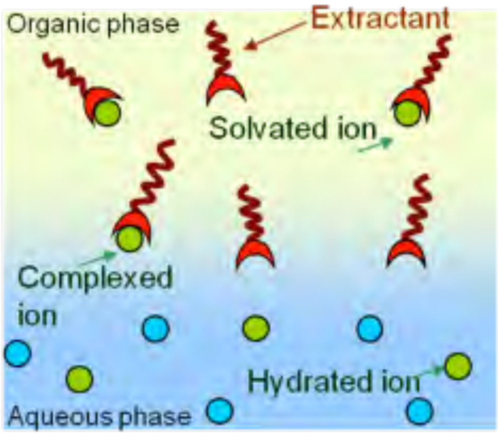

Figure 1 Remediation process by complexation at liquid interface.

Such a study often starts with an initial stage where the complexation reaction is investigated, and this may be performed at the air-water interface, like in the study [1] presented here. A molecular organic chromophore, PalmitateLuciferin, has been synthesized for studying ion complexation at the air-water interface using **Second Harmonic Generation** (SHG). The SHG technique, with a high surface sensitivity, is one on the most adapted technique to study the active interfacial behavior at the molecular scale. The molecule PalmitateLuciferin, was designed through the addition of a long hydrophobic palmitoyl alkyl chain to the aromatic π- electron system of Luciferin. We first demonstrate that this organic chromophore is a potential candidate for SHG studies of ion complexation with the measurement of its first hyperpolarizability in aqueous solutions by Hyper Rayleigh Scattering (HRS) with and without calcium ions. Then, we characterize the PalmitateLuciferin surfactant properties at the air-water interface combining surface tension measurements with a surface SHG study and Brewster angle imaging. These results allow us to build a molecular description of the chromophore at the interface and observe its molecular re-organization during the monolayer compression leading to the formation of aggregates. Finally, we show that the initial goal of the designing work is achieved since PalmitateLuciferin indeed exhibits a higher SHG response in the presence of calcium ions in the aqueous sub-phase as expected.

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Preparation of γ-AlOOH loaded-zeolites and characteristics for phosphate adsorption

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Phosphorus is one of the most important elements leading to water eutrophication, meanwhile, phosphorus is one of the non-renewable available resources. People have paid more attention to the removal and recycling of phosphorus in wastewater treatment. In this study, one kind of modified zeolites, zeolites loaded with γ-AlOOH (γ-AlOOH-Z), was prepared with precipitation of $AlCl_3$ and used to adsorb phosphate from the wastewater. Under the optimal preparation conditions, aluminum was loaded on zeolites (with a particle size of 100-120 mesh) with a loading amount of 116.1 mg/g, and the phosphate adsorption capacity of γ-AlOOH-Z reached 16.16 mg/g, which increased by 87.5% compared with that of the natural zeolites. XRD patterns showed that pure γ-AlOOH were successfully loaded on the natural zeolites, and the preparation conditions including temperature, pH, time significantly affected the loading of γ-AlOOH and species of aluminum, further impacted the phosphate adsorption. Electrostatic interaction and ligand exchange were the main mechanisms of phosphate adsorption onto γ-AlOOH-Z, and the ligand exchang between surface hydroxies and phosphate ions was the main one. Five cycles of adsorption-desorption process showed that desorption efficiency maintained at about 95%.

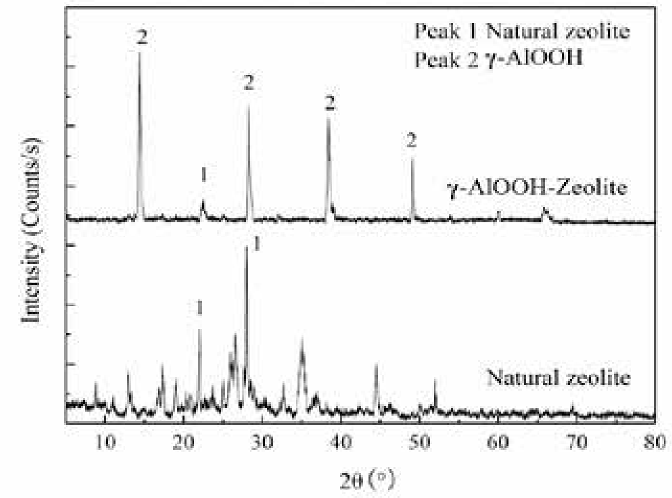

Figure 1 X-ray diffraction patterns of γ-AlOOH-Z under the optimal preparation conditions and natural zeolite

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Removal efficiency of high concentration waste water using Capacitive Deionization Process

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The volume of usable fresh water has been decreasing globally due to pollutions of river and underground waters. The pollution of underground water, resulted from phosphate and nitrate ions, eutrophicated. For the prevention of these problems, the need to disposal of nitrate and phosphate ion is currently growing day by day. This study is to confirm ion adsorption properties of nitrate ions and phosphate ion in high concentrate-synthetic waste water by using CDI(Capacitive Deionization) process.

CDI cell was fabricated to confirm ion adsorption properties, and synthetic waste water made of 5,000ppm NH_4-N, 4,000ppm NO_3-N, 3,000ppm PO_4-P is used. In experiment method, batch type of charging 1 minute and discharging 3 minutes proceeded after inflow of synthetic waste water into CDI cell. Charging and discharging as 1 cycle, 40 cycles proceeded, and then treated waste water which drained out from discharge process analyzed with sampling.

This study researched on ion adsorption properties for elimination of nitrate and phosphate ion in high concentrate-synthetic waste water using CDI process. As a result, it was confirmed that NH_4-N, NO_3-N, PO_4-P are respectively 79.61%, 72.10%, 73.97% adsorbed.

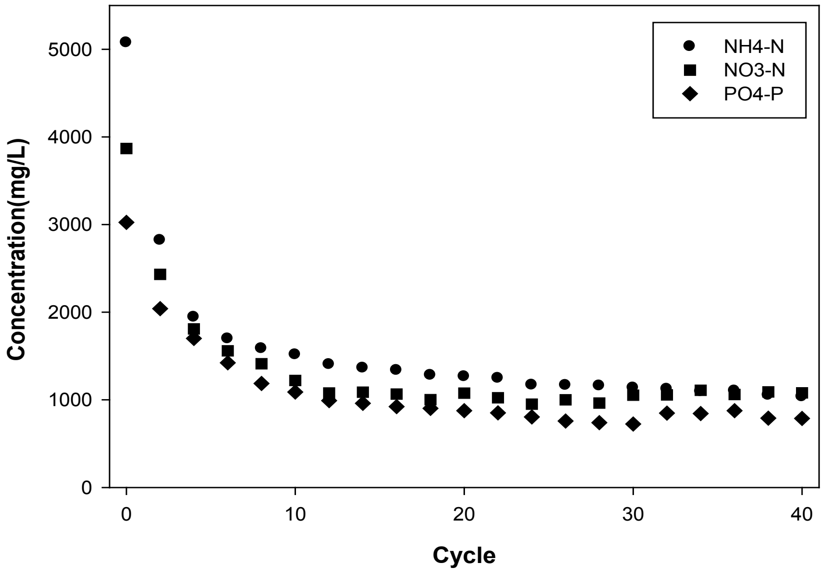

Figure 1 Variation of NH_4-N, NO_3-N, and PO_4-P concentration during the adsorption

Batch mode and continuous membrane capacitive deionization using flowing carbon electrodes

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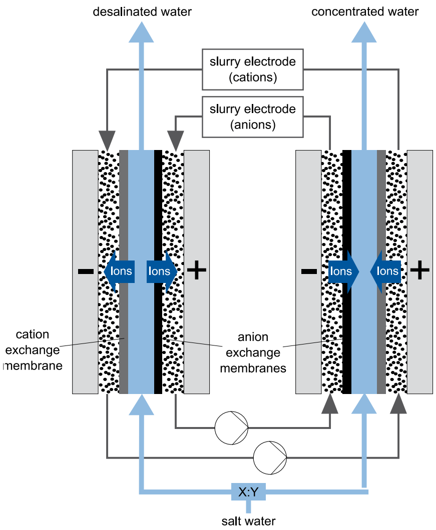
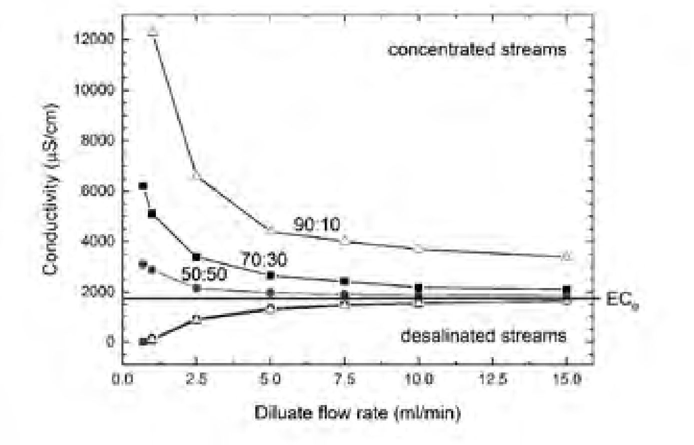
Continuous water desalination using Membrane Capacitive DeIonization (MCDI) process assisted with flowing carbon electrodes is reported. Batch-mode experiments showed extremely high salt adsorption capacities of 260 mg/g for the flowing activated carbon electrodes. A continuous process comprised of desalinating and concentrating MCDI units and two recirculated flowing electrodes was operated at 50, 70 and 90% feed water (1gNaCl) split ratios. Desalination rates of more than 99% were achieved at > 90 % water recovery, and were independent on the diluate/concentrate flow rate ratio.





Hyper Salinity Desalination using Atlantis RDI Capacitive Deionization Technology

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Atlantis Technologies has developed the next generation capacitive deionization technology that enables the practical desalination of industrial waste water exceeding 100,000 mg/l salinity. The technology was developed in California for use on industrial waste waters such as oil/gas produced water, supersaturated mining water, and flue gas desulfurization waters generated by coal fired power plants. This is possible through dramatically increased flux rates, extended capacitors flow lengths, and unique system operation which together increase the range of applications by a factor of 10 - 20. Our presentation will showcase lab and field studies, flux rate characterizations, and system design.

Capacitive Deionization for Waste Water Re-use: Energy Efficiency Considerations

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Due to the always increasing worldwide water scarcity associated to the climate change there is the need to increase the reinjection of wastewater into the overall water cycle. The reuse of treated waste water has been identified as a potential way for addressing long term imbalances between water demand and water supply, therefore reducing the vulnerability of water and environmental resources to climate change and man-made pressures. This study provides a mechanistic analysis of Capacitive Deionization (CDI) applied on Waste Water Re-use, paying special attention to Energy Efficiency aspects. CDI technology is gaining increased scientific interest since 2006 [1]. However, not too many publications indicate the feasibility of the kWh/m3 consumption in CDI systems. The common assumption proposes that the main problem may be the ions adsorption capability of the electrode material during charging [2]. To our experience, desorption processes may be even more problematic, in energy efficiency terms, since they hold diffusional difficulties when submitted to relatively high current densities [3].
This work provides an overview of current strategies for operating these systems aiming to improve energy recovery and lead this process to the point of making these systems an option for use in waste water treatment plants. Experimental work includes consecutive deionization – regeneration tests conducted under a combination of constant current and constant voltage steps at different current rates (close to real life scenarios). A schematic representation of the performance profile proposed can be seen in Figure 1 (left) [4].

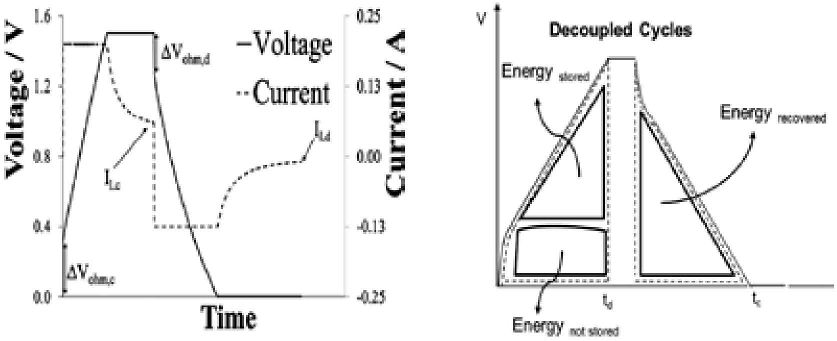

Figure 1 Charge-discharge configuration in decoupled procedures (left). Energy components in decoupled cycles (right). [4]

As result, in order to further optimize efficiency in the CDI process, particularly for 2 000 – 20 000 ppm waste water concentration, we are systematically improving strategies for operating these systems in such a way to achieve major impact on the practical application of this technology [4].

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ORAL PRESENTATIONS TUESDAY

Role of Surfaces in the Biochar Effect

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Intensive research in the last decade into agronomic impacts of soil amendment with biochar, the solid co-product of biomass pyrolysis, has revealed that many soil chemical and biological characteristics may be altered when biochar is added to soil: pH, Eh, microbial diversity and community structure, greenhouse gas emissions, nutrient retention, soil physical structure, water retention, and more. These changes can affect plant growth, productivity, and resistance to stress when grown in biochar-amended media. A major challenge today is to understand which biochar characteristics are responsible for this "Biochar Effect". Biochar surfaces are highly heterogeneous and reactive, and interactions occurring at or being promoted by those surfaces may play a role in many of the observed effects. For example, biochar surfaces have a relatively high content of pH-dependent cation exchange sites [1], and this content increases as biochar ages in the soil. This means that biochar absorbs cationic nutrients such as NH_4^+, and also releases them for plant utilization; retention capacity for cations increases as biochar ages in the soil. In contrast, biochar has virtually no anion exchange capacity, meaning that nutrients such as NO_3^- and PO_4^- are not retained as anions. Reduction reactions promoted by biochar surfaces and biochar-borne phenolic compounds and humic-like substances can cause dissolution of soil Fe and Mn oxides, releasing these nutrients into solution [2]. Biochar-derived, water soluble humic-like substances can complex with these released elements much as do humic and fulvic substances, increasing their plant availability. Redox active biochar surfaces and molecules can promote microbial activity by acting as electron shuttles. Biochar surfaces adsorb pathogenic enzymes and toxins, helping to protect plants, and the adsorbent surfaces can interact with plant root exudates changing the profile of those exudates in the soil and hence the microbial community structure [3]. These and many other attributes of biochar surfaces can make important contributions to biochar effects in the soil.

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Phosphate adsorption on hydrous ferric oxide and its effect on the re-growth of broken flocs

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Phosphate adsorption on hydrous oxide flocs is important for aquatic environmental processes and in the treatment of water with hydrolyzing coagulants. Removal of phosphate from surface waters can be achieved either by adsorption on suitable adsorbents or by chemical precipitation. Under most practical conditions, hydrolyzing coagulants, such as salts of aluminium or iron(III) produce an amorphous precipitate of the hydrous oxide which can be very effective in the removal of both particulate and soluble impurities, the latter including dissolved organic material and phosphates.

In the present work a systematic study has been carried out of the interaction of orthophosphate with hydrous ferric oxide (HFO) precipitate, at different pH values and with fresh and aged precipitate. HFO is initially precipitated as very small particles a few nm in size, which can then aggregate to form much larger flocs (up to several hundred μm). In the absence of phosphate, stirring of flocs at high shear causes some reduction in pH, which is most significant in the pH range 8-10. As has been previously found, phosphate adsorption decreases with increasing pH and is significantly lower after aging of the precipitate. At pH values greater than 5, phosphate adsorption on HFO causes an increase in pH, indicating binding of H^+ or release of OH^-. By a pH-controlled titration procedure, the change in OH^- concentration could be determined for a range of phosphate additions. These were compared with the amounts of phosphate adsorbed under the same conditions. The results showed significant effects of both pH and precipitate age.

Adsorbed phosphate has a major influence on the growth of flocs. Depending on pH and phosphate concentration, floc growth may be either enhanced or imhibited. Breakage of HFO flocs by high shear is known to be irreversible to some extent, so that broken flocs do not re-grow completely after the shear is reduced. It has been found that addition of phosphate during floc breakage can entirely prevent re-growth and this is closely related to phosphate adsorption. By considering the nature of surface groups on HFO and the nature of bonding within HFO flocs a model for the breakage and re-formation of flocs is proposed, which can explain the irreversible nature of floc breakage. The role of phosphate in this process will also be considered.

Effect of phosphate sorption on Ferralsol dispersion: Evaluation with stability ratio and repulsive potential energy

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Soil dispersion induces soil erosion and colloidal leaching. The phosphate (P) sorption results in increase of net negative charge. The influence of phosphate on soil dispersion must be evaluated well in order to control soil erosion and leaching. In this study, influence of P sorption on Ferralsol soil dispersion was investigated by calculating repulsive potential energy based on zeta potential and stability ratio of soil suspension. Ferralsol which is a typical soil in rainy tropical region was used as the material. We have used monovalent (Na) and divalent (Ca) ions in 1mmol$_c$ L^{-1} equilibrium salt solution. The batch method of phosphate sorption experiments was conducted at different pH 4, 5.5, 7 and 8.5 by adding NaH_2PO_4 or $Ca(H_2PO_4)_2$. Salt concentration was supplemented by $NaNO_3$ or $Ca(NO_3)_2$ when the adding phosphate concentration was less than 1 mmol$_c$ L^{-1}. Salt concentration increased when > 1mmol L^{-1}P was added in some cases. Stability ratio (W), derived from dynamic light scattering method, was used to evaluate stability of colloid suspension. Stability ratio was calculated by k^f/k; k^f is the rate of fast coagulation and k is the coagulation rate of the sample under consideration. The repulsive potential energy between the soil colloids when they approach at 1 nm was calculated using the zeta potential and the diffuse double layer theory. Generally, the stability ratio increased with increasing pH because the negative charge of the soil increased with increasing pH. In Na system, the stability ratio increased when P sorption increased up to around 10 mmol P kg^{-1}. When P was sorbed, the soil charge became more negative and the soil dispersed well due to the electric repulsive force. After the peak, it decreased with increasing P sorption at > 10 mmol P kg^{-1} because of the increase of electrolyte concentration (>10 mmol$_c$ L^{-1} Na). In Ca system, similar trend was observed. However, the stability ratio increased again at around 250 mmol P kg^{-1} at pH 7 & 8.5 probably because of the decrease of electrolyte concentration after Ca-P precipitation. Stability ratio increased with the increase of repulsive potential energy (Fig. 1). The stability of the soil was evaluated with the repulsive potential energy. In Na system, the soil flocculated well when the repulsive potential energy was < 0.1 μJ m^{-2}, corresponding with logW <1.15. Soil dispersed well when logW >1.4 at repulsive potential energy >0.19 μJ m^{-2}. In Ca system, at the energy <0.06 μJ m^{-2} the soil flocculated well (logW<0.17). At the energy >0.36 μJ m^{-2} the soil dispersed well (logW>1.14).

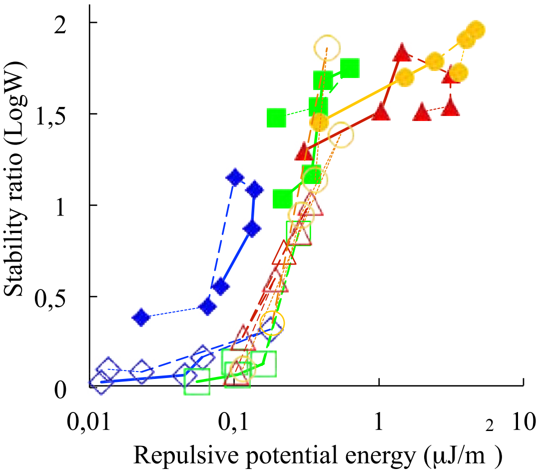

Fig. 1 Repulsive potential energy and stability ratio

◇pH 4, □pH 5.5, △pH 7, ○pH 8.5 for $Ca(NO_3)_2$ concentration

◆pH 4, ■pH 5.5, ▲pH 7, ●pH 8.5 for $Na(NO_3)_2$ concentration

.... electrolyte concentration ≤ 1 mmol$_c$ L^{-1}

- - - - - 1 mmol$_c$ L^{-1}< electrolyte concentration ≤ 10 mmol$_c$ L^{-1}

______ electrolyte concentration >10 mmol$_c$ L^{-1}

Plasma Polymer Coated Particles: A New Class of Adsorbents for Water Purification

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In recent years, functionalized hydrophobic materials have attracted considerable interest as petroleum hydrocarbon removal agents. This investigation has applied plasma polymerization as a novel, green and one-stage process [1] to develop nanostructured hydrophobic and oleophilic films for water purification. 1,7-Octadiene was plasma polymerized onto silica particles using a radio frequency inductively coupled reactor fitted with a rotating chamber. Plasma polymerized 1,7-octadiene (ppOD) films were deposited using a varied range of plasma power, 1,7-Octadiene flow rate and deposition time. The surface chemistry of ppOD coated particles was investigated via X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectroscopy, while Washburn capillary rise measurements were applied to evaluate the hydrophobicity and oleophilicity of the particles. The effectiveness of ppOD coated particles for the removal of hydrophobic matter from water was demonstrated by adsorption of motor oil, kerosene, and crude oil. Petroleum hydrocarbon removal was examined by varying removal time and particle mass. The morphology of oil loaded ppOD coated particles was examined via environmental scanning electron microscopy observations. Increasing the polymerization time increased the concentration of hydrocarbon functionalities on the surface (Fig. 1), thus also increasing the hydrophobicity and oil removal efficiency (ORE) [2,3]. The ppOD coated particles have shown to have excellent ORE. These particles were capable of removing 99.0–99.5% of high viscosity motor oil in 10 min, while more than 99.5% of low viscosity crude oil and kerosene was adsorbed in less than 30s. Plasma polymerization has shown to be a promising approach to produce a new class of materials for a fast, facile, and efficient oil removal.

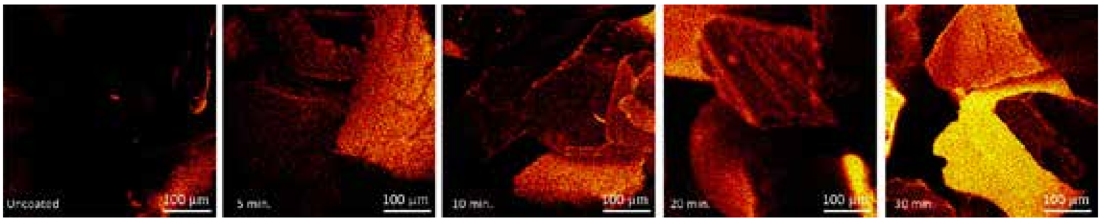

Fig. 1. ToF-SIMS CH^- ion maps for uncoated and coated particles for different times

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Keynote
Characterization of droplets produced by electrospray emulsification

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Electrohydrodynamic atomization (EHDA) provides a novel way to enhance the dispersion of droplets in a liquid media, therefore to create highly homogeneous (droplet size) emulsions. emulsion and improve its quality. The effectiveness of this technique is already proven by some authors (see reference list) and was further investigate in this work regarding its capability to produce micro size, well dispersed and highly charged droplets emulsions. Various liquid-liquid combinations were selected. The liquid combinations were initially tested to identify which could produce a stable cone-jet mode, i.e. small size droplets with narrow distribution. After selecting the most appropriated liquid combinations, the produced emulsions were further characterized in terms of the droplet diameter and size distribution, the emulsion quality, electrical energy requirements. Additional studies were performed to study the suitability of applying theoretical scaling laws to predict the droplet size and spray current. One of the selected liquid combinations, e.g. ethylene glycol-hexane, was found to generate stable cone-jet mode between 6 and 8 kV for a range of flow rate of 0.5- 4.0 mL/h. In this mode, the measured average droplet diameter was found to range from 2- 14µm and a bimodal size distribution was observed. The droplet dispersion into the continuous phase was enhanced by the electric field and by self-repulsion. The stability of the droplets in the continuous phase was found to increase in the presence of a surfactant (Tween 80). Preliminary results showed that the electric energy requirements were in the scale of 106J/m3. The average droplet diameter was found to scale with the liquid flow rate as in d~Q0.33 and the dimensionless current scaled with the flow rate by I/I0~ (Q/Q0)0.5. The study has, therefore, indicated that EHDA can be effectively used in the preparation of emulsions.

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Simultaneous production of high quality water and electrical power from aqueous feedstocks and waste heat by high pressure membrane distillation

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A new membrane distillation concept (MemPower) has been developed for the simultaneous production of high quality water from various aqueous feedstocks with cogeneration of mechanical power (electricity). Driven by low grade waste heat a pressurized distillate can be produced by operating TNO's Memstill®-process at high hydraulic pressures. These pressures are theoretically limited by the Liquid Entry Pressure (LEP) of the membrane. The proof of principle has been shown and is based on the transport of water vapor against a hydraulic pressure gradient. Various existing and new types of membranes have been evaluated in order to obtain high yields in water flux and power densities. Power densities have been measured which are sufficient to drive the pumps in membrane distillation. This allows standalone Memstill-units without electricity consumption to be possible, which are fully driven by waste heat. The application of new incompressible hydrophobic membranes, combining a high permeance with a high LEP, will allow for much higher power densities.

Investigating the fouling stages during membrane filtration of silica nanoparticle solutions

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In the last decade many new nanotechnology based products have been developed. This causes a world-wide exponential growth in the production volume of nanoparticles (NPs). The impact of manufactured NPs on living organisms is still under discussion. However, most researchers suggest that NPs are toxic. It is obvious that after usage the manufactured NPs will accumulate in the aqueous environment. Therefore, sustainable growth of nanotechnology requires an environmentally-friendly technology to remove NPs from potential drinking water sources. A promising technique to remove nano-sized contaminants from water is based on membranes. However, not much is known on the filtration and fouling behavior of NPs in membrane processes.

Ultrafiltration and especially microfiltration membranes are prone to internal fouling and pore blockage caused by the presence of NPs having a diameter smaller than the pore size of the membrane applied. The small size of NPs results in a high surface area to volume ratio, which significantly enhances the role of surface interactions on the stability of the NP suspensions. On the other hand, the stability of NP suspensions and in fact their tendency to aggregation strongly affect the fouling mechanism during membrane filtration of the NPs.

In this experimental study, fouling and rejection of mono-dispersed model NPs were investigated. A microfiltration hollow fiber membrane was employed in dead-end filtration mode for the filtration of commercially available silica nanoparticles under constant pressure. Applying a low concentration of NPs and a large difference between the membrane (~200 nm) and the nominal size of the NPs (22 or 7 nm) allowed detailed investigation of the fouling mechanisms. Base on filtration and rejection data, four fouling stages were proposed: adsorption, electrostatic blockage effect, pore blocking, and cake filtration. The occurrence and character of these stages were strongly affected by the ratio between particle size and pore size. Furthermore, it was found that solution properties like the presence of salts, the pH or the valency of the cation strongly alter fouling and rejection behavior. The observed effects of the solution properties was explained using the DLVO theory, which describes colloidal stability and the role of solution properties. Lower repulsive interactions between the nanoparticles accelerate fouling by faster pore blockage and aggregation on the membrane surface. The rejection of the NPs was improved by instantaneous pore clogging and formation of a deposit on the top of the membrane surface. Porosity of the filtration cake layer on the membrane surface was strongly dependent on the NPs solution properties. This paper clearly shows that the filtration of NPs can be optimized by choosing the right practical conditions.

Transport of Sewage-borne Ammonium in a Floodplain Aquifer: Column Experiments with Aquifer Materials from the Yamuna Floodplain in Delhi (India)

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The Yamuna River is the biggest tributary of the Ganga River in the Indo-Gangetic plain and it flows through the mega city Delhi in North-South direction. Owing to a fast growing population, the river stretch in Delhi is highly influenced by untreated or partially treated sewage water. Dissolved oxygen concentrations in the river are often below 1.0 mg/L during the winter months and the prevailing form of nitrogen is ammonium, which was measured in concentrations of up to 20 mg/L in 2012/13. In recent years, elevated ammonium concentrations were observed at a riverbank filtration site in central Delhi, which was constructed in 1973. Here ammonium concentrations of up to 30 mg/L were measured in hand pumps at a distance of 250 m to the riverbank and concentrations between 5 and 8 mg/L were found in a large horizontal collector well (Ranney well) at a distance of 500 m to the river during normal well operation.

Due to cation exchange reactions, ammonium is generally retarded in the groundwater flow. Transformation or degradation of ammonium can occur along the flow path as nitrogen is a redox sensitive species and ammonium oxidation can take place (either anoxic – anammox, or oxic – nitrification). Furthermore, the permanent fixation of ammonium in the sediment can also remove ammonium from the system. Mineralization of organic nitrogen can be an additional source of ammonium (Repert et al. 2006). These processes are all strongly related to the sediment characteristics and thus a quantitative prediction of future ammonium concentrations is not possible without knowing the site-specific ammonium-sediment interactions.

Column experiments were conducted with artificial oxic and anoxic groundwaters and aquifer material from different representative zones of the aquifer, which has a thickness of 17 m and consists of a bottom gravel layer and overlying medium grained sands which tend to be more fine-grained towards the top. Results show that sediments from a distance of 35 m and 250 m from the riverbank are in equilibrium with the groundwater, whereas disequilibrium between adsorbed ammonium on the exchanger and ammonium in the groundwater can be observed at 500 m distance, indicating that this is the current front of the ammonium plume. In the adsorption and desorption experiments, the predominant process observed in the deeper sediments from depths > 25 ft (gravel and sand) was cation-exchange (sorption and desorption), with gravel showing slower reaction kinetics than the sand (30 vs. 15 flushed pore volumes to release all adsorbed ammonium). This was unexpected and the reason for the retardation is still under investigation. Only in the very top layer of the aquifer at a depth of 3 m degradation or fixation of 30-55% of the ammonium input was detected.

The results of the column experiments will be used to set up a 1D reactive transport model for the transport of ammonium at the field site in order to model future water quality scenarios. This is necessary to evaluate the suitability for future drinking water production and to plan appropriate treatment options.

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9.50 - 11.10
BENTACERA ZAAL

Tuesday

Ion adsorption at mineral-electrolyte interfaces probed by high resolution Atomic Force Microscopy

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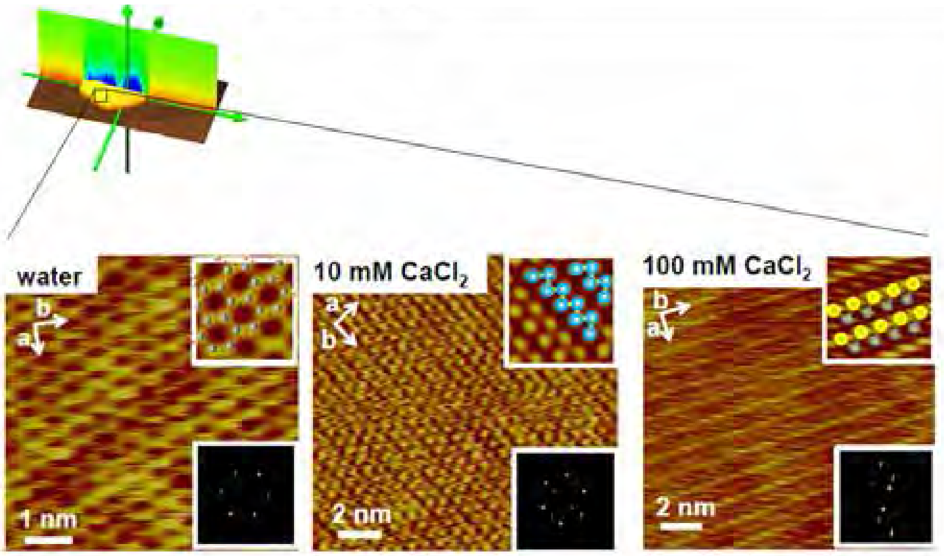
The distribution of ions and charge at solid-water interfaces plays an essential role in a wide range of processes in biology, geology and technology. While theoretical models of the solid-electrolyte interface date back to the early 20th century, a detailed picture of the structure of the electric double layer has remained elusive, largely because of experimental techniques have not allowed direct observation of the behaviour of ions, i.e. with subnanometer resolution. We have made use of recent advances in Atomic Force Microscopy (AFM) to reveal, with atomic level precision, the ordered adsorption of the mono- and divalent ions that are common in natural environments to heterogeneous gibbsite/silica surfaces in contact with aqueous electrolytes. Complemented by density functional theory, our experiments produce a detailed picture of the formation of surface phases by templated adsorption of cations, anions and water, stabilized by hydrogen bonding. In particular, we demonstrate the sequential build-up of the Stern layer by consecutive adsorption of Ca^{2+} and Cl^- ions upon increasing the bulk concentration of $CaCl_2$. Simultaneous measurements of the charge in the diffuse layer using AFM spectroscopy suggest that deprotonation of hydration water largely compensates the charge due to cation adsorption.



Pore-scale study of processes and transport in porous media; an overview

T. Sweijen, S.M. Hassanizadeh, N. K. Karadimitriou, Q. Zhang

Utrecht University; Department of Earth Sciences, The Netherlands

Website: http://www.geo.uu.nl/~wwwhydro/

To increase our insight of flow and transport phenomena in porous media on both micro- and macro scales, pore-scale studies are essential. Studies have included chemical, biological, and physical applications. Experimentally, micro-models have been proven to be a valuable tool as they allow the observation of flow and transport phenomena on the micro-scale. A micro-model is an artificial representation of a porous media, made of a transparent material. We have used Poly-Di-Methyl-Siloxane (PDMS), which is a viscoelastic, silicon-based organic polymer. It is optically transparent, inert, non-toxic, and non-flammable. We have performed two-phase flow and colloid transport experiments in these micro-models. We have established that the inclusion of fluid-fluid interfacial area allows for the modelling of the hysteretic relationship between capillary pressure and saturation in porous media. In other words, data points of capillary pressure-saturation-interfacial area from many (scanning) drainage and imbibition experiments fall on a single surface. In colloid transport experiments, we directly observe colloids movement, their retention at interfaces between phases, and their mobilization by moving interfaces and contact lines.

Another valuable tool is pore-scale modeling, which allows us to conduct numerical “experiments”, from which closure equations for macro-scale description can be obtained. Currently, we are using a Discrete Element Method to study the coupling between swelling porous media and pore fluid flow.

The Dynamics of Micro-vortices During Overlimiting Electrodialysis

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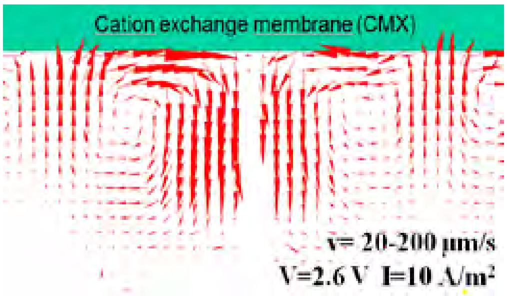
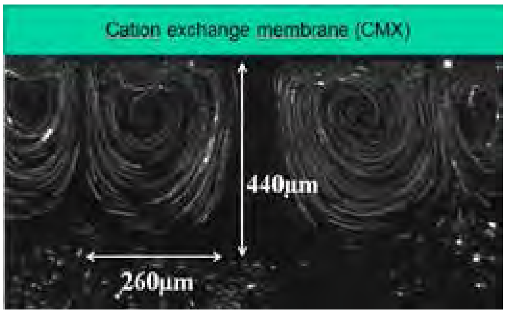
We experimentally investigate the coupled dynamics of global ion-flux and local hydrodynamics of an electrolyte solution close to a charge selective membrane under an electric forcing. At small voltages, cations transport diffusively across a cation exchange membrane (CEM), whereas the transport of oppositely charged anions is blocked, causing the main resistance of the system. At higher voltages this resistance suddenly increases and in addition to diffusive transport, hydrodynamic convection sets in within a boundary layer of O(100 µm), resulting in the so-called over-limiting current. In this regime we measured the fluid flow with particle image velocimetry (PIV) combined with chronopotentiometric resistance measurements for the first time. Our results reveal that the micro-vortices are caused by gravitational unstable gradients and by electro osmotic-coupling between the membrane surface and the solution. Moreover, under a constant applied electric current, the electroconvective micro-vortices start with a voltage jump and grow linearly both in size and speed. After this initial linear growth, the resultant voltage levels off around a fixed value. The average vortex size stabilizes as well, however the individual vortices are unsteady and dynamical. Our experimental setup and results offer a complete picture of the coupled dynamics of the hydrodynamics and electrical responses of an electrolyte, beneficial for characterizing a variety of charge selective membranes in order to improve electrodialysis desalination processes.





Water Purification and Brine Concentration by Shock Electrodialysis

Sven Schlumpberger[1], Matthew Suss[1], Daosheng Deng[1,2], Ali Mani[1,3], Martin Z. Bazant[1,4]

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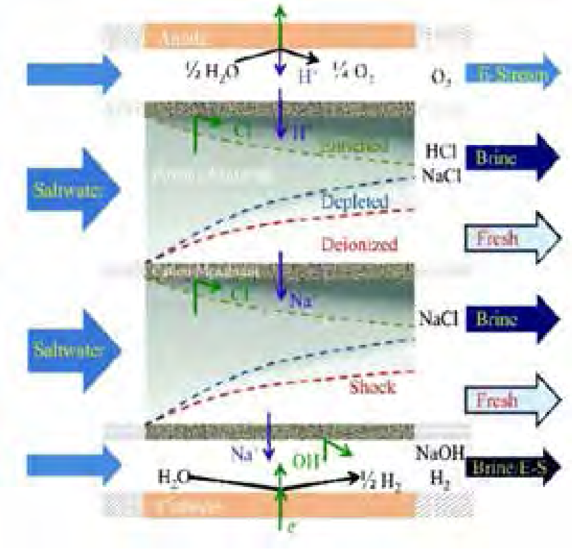
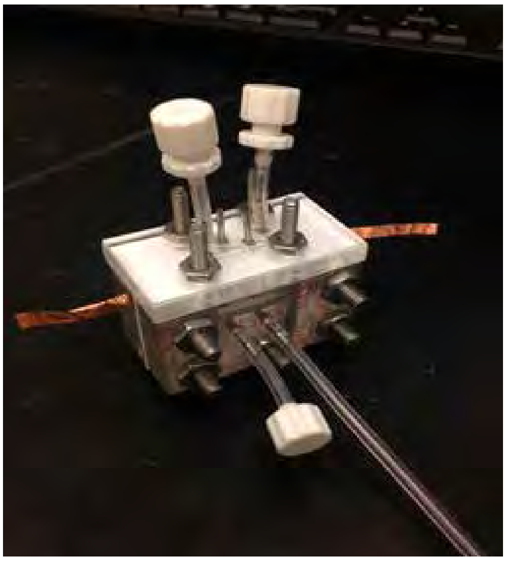
In this project, we investigate experimentally and theoretically the possibility of exploiting deionization shocks in porous media for water purification and brine concentration by "shock electrodialysis". The basic idea of this new approach is to drive an over-limiting current (faster than diffusion) through a charged porous medium sandwiched between two cation-exchange membranes, perpendicular to a pressure-driven cross flow, which produces a sharp "shock" in the salt concentration profile between deionized and concentrated steams, which are separated at the outlet. In contrast to classical electrodialysis, only one membrane type is needed to trigger the phenomenon, and the separation is effectively "membraneless" within the porous medium. Boundary layer analysis, generalizing the Leveque solution for over-limiting current, provides useful engineering principles, and detailed simulations of the system help us gain insight into the phenomena at play. We demonstrate the principles of shock ED experimentally in a sequence of prototypes. Initially we use copper electrodes and copper sulfate solution to demonstrate the feasibility of the project and then replace the copper electrodes with electrode streams sustaining the current by water electrolysis, as in traditional ED, in order to be able to use this phenomenon to remove a wide range of electrolytes, including sodium chloride, from water. The results show reasonable efficiency and unique separation capabilities, such as removal of particles and disinfection, that may find applications in compact water treatment and brine concentration.





Dynamic adsorption of pharmaceutical residues at trace concentrations onto activated carbon cloths

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Several studies have shown the occurrence of pharmaceutical residues into various aquatic compartments [1-2]. This pollution is not totally removed by the usual treatments. Some compounds like diclofenac or carbamazepine are thus found in drinking waters. Adsorption processes (using activated carbons) are promising to remove these undesirable compounds from raw waters. Furthermore, activated carbon fiber cloths (ACFC) have shown many advantages for water treatment [3] since these adsorbents possess high specific surface areas, and more particularly, narrow pore size distributions, which enhance their affinity and selectivity towards these pollutants at trace concentrations.

The first part of our study dealt with the determination of adsorption kinetics and isotherms for four different chemical species (acetaminophen, caffeine, diclofenac and carbamazepin). These experiments were carried out using batch reactors but with environmental conditions (i.e. initial concentrations of 1 µg/L and in the presence of natural organic matter). Therefore, maximum adsorption capacities were determined as well as an efficient isotherm models (Langmuir-Freundlich). The competition with other organic molecules was especially critical when dealing with trace concentrations of the targeted compound. If the natural organic matter have a low impact on adsorption capacities at high concentrations, the impact is very important at the lowest aqueous concentration (up to - 60 % of the single-component adsorption capacity). Parting addition, the competition with the organic matter involved a large decrease of the adsorption rate. More precisely, the most impacted coefficient for mass transfer is the surface diffusivity (from the application of the homogeneous surface diffusion model).

Following this first approach (in batch conditions), the second part of the study focused on the dynamic adsorption of the four compounds. Breakthrough curves were determined using an experimental unit that was designed for a maximum flow rate of 100 L/h and inlet concentrations of the pharmaceutical residues of 1 µg/L. Various operating conditions were tested and their influence was evaluated: the type of water (tap water, surface water with different contents of natural organic matter), the velocity of the liquid through the filter, the thickness of the filter (i.e. the number of layers of ACFC), and the type of ACFC. The adsorption in dynamic conditions was then compared with the characteristics obtained in the batch experiments (mass transfer coefficients, adsorption capacities, influence of the competitions).

Adsorption of chitosan from aqueous solutions onto silica

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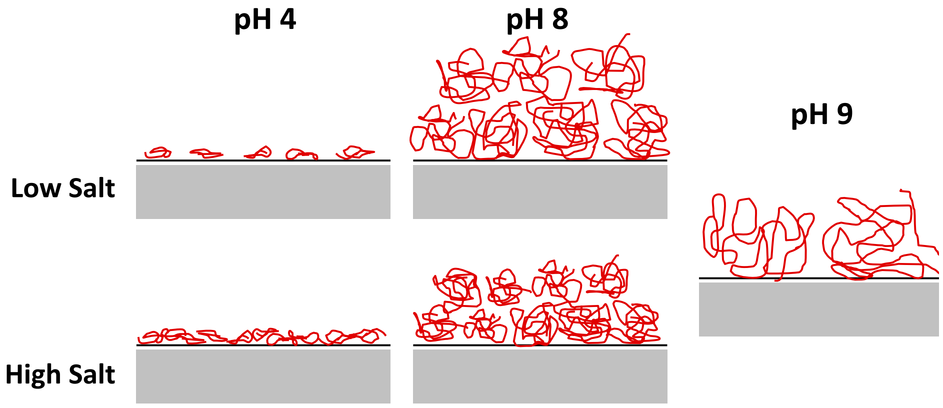
Chitosan is the only cationic polymer originated from natural sources and is widely employed as a biomaterial for numerous systems and in the most diverse fields. Few studies address the fundamental question of the adsorption mechanism of chitosan on negatively charged surfaces. However, an understanding of this adsorption behavior is important to the rational design and to the advancement of the environmental and engineering systems applying chitosan as a functional material.

We present the adsorption behavior of chitosan onto silica from aqueous solution. The adsorption behavior and the resulting layer properties are investigated by combining optical reflectometry and the quartz crystal microbalance. The same surfaces are used to measure the amount of adsorbed chitosan with both techniques, allowing the systematic combination of the respective experimental results. Therefore, we determine layer thicknesses and their water content for chitosan adsorbed on silica from aqueous solutions of varying composition. In particular, we study the effect of pH at 10 mM NaCl and we focus on the influence of electrolyte type and concentration for two representative pH conditions.

In mildly acidic solutions, chitosan behaves like a weakly charged polyelectrolyte, whereby electrostatic attraction is the main driving force for adsorption. Under these conditions, chitosan forms rigid and thin adsorption monolayers with an average thickness of approximately 0.5 nm and a water content of roughly 60%. The tendency of chitosan to form highly swollen and relatively large aggregates is confirmed in neutral solutions, whereby adsorption layers become significantly thicker (~10 nm) as well as soft and dissipative. These films are also characterized by a highly hydrated state containing up to 95% of water.

This study demonstrates that chitosan forms stable adsorption layers on oppositely charged silica surfaces under a wide range of chemical conditions. Significantly different films can be obtained by fine tuning the adsorption conditions. In particular, the possibility to produce tailored adsorption layers simply by adjusting the solution pH represents a remarkable opportunity to use this polyelectrolyte in a variety of systems targeted for different purposes.



Sacrificial polymer layers for easy membrane cleaning

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Fouling constitutes a major problem in membrane technology and leads to a reduced production capacity and increased operation cost. This research presents a solution for membrane fouling based on a polymeric “Sacrificial Layer” approach. One of the options available to control fouling is surface modification of the membranes. To modify and tune the surface of an ultrafiltration membrane with desired properties the most promising method seems to be the layer-by-layer (LbL) electrostatic self-assembly leading to polyelectrolyte multilayer (PEMs) formation [1]. PEM are coated using LbL approach involving alternating sequential adsorption of polycations and polyanions onto a charged surface. The number of deposited layers determines the thickness of a PEM membrane (PEMM) and thus selectivity and flux can be tuned by the number of LbL cycles or by the chemical composition of the utilized polyelectrolytes (PEs) [2]. Now the PEM layers of a few nanometers thickness can also be removed by simple trigger such as a change in pH or salt concentration. This so-called “sacrificial layer” approach, allows the possibility that when fouling agents get adsorbed on the surface of the membrane, they can be removed by simply desorbing (sacrificing) the polymer coating in solution. An extra benefit might be that the polyelectrolytes that are released into solution upon destruction of the layer could well act as so-called anti-redeposition agents: by adsorbing to the released fouling agents they could prevent possible re-adsorption of the fouling agents. This concept is schematically shown in Fig. 1. To give a “proof of principle” for the application of such multilayers as sacrificial layers for membrane technology we use polyelectrolyte multilayers in combination with model foulants such as silica particles and BSA (bovine serum albumin). Such proof of principle of the sacrificial layer approach has been provided for a silicon substrate [3] but not yet for applied systems such as membranes. We investigate the growth of a new LbL system including the interaction with model fouling agent via reflectometry. Then to sacrifice these layers, including the fouling agent, the effect of appropriate trigger (based on low pH and a high salt concentration) will be discussed. We demonstrate the effectiveness of the approach both on model surfaces and on a hollow fiber ultrafiltration membrane. To check the efficiency of the modified membrane, permeability and retention results will be discussed along with the effect of trigger

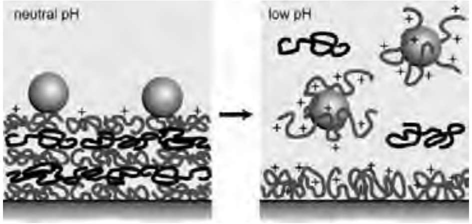

Fig. 1. Schematic representation of polyelectrolyte multilayer as a sacrificial layer. Fouling agents are adsorbed to the multilayer but upon a change of the pH, the layer desorbs, taking with it the adsorbed fouling particles. Released polyelectrolytes cover the particles and prevent re-adsorption.

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Colloidal flocculation of PSL particle induced by an adsorption of polyelectrolyte studied in relatively concentrated suspension

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Flocculation of polystyrene latex (PSL) particles induced with oppositely charged polyelectrolytes are investigated near the regime of optimum flocculation concentration (OFC) as a function of ionic strength and colloid concentration. Flocculation is performed by mixing of 5 ml colloidal dispersion with same amount of polyelectrolyte solution by end-over-end. Results were evaluated by eventual sediment, electrophoresis and microscopic observation of floc morphology. The sedimentation test revealed that separation by flocculation is practically induced only in the limited range of polyelectrolyte dosage around OFC over which the colloidal dispersion is stabilized by the effect of reversed charge due to absorbed polyelectrolytes. It was confirmed that the condition of OFC corresponds to the condition where the charge of colloidal particle is electrokinetically neutralized by the adsorption of oppositely charged polyelectrolyte irrespective of ionic strength and colloid concentration (Fig.1). Narrow and sharp window of separation around OFC is observed under low ionic strength, while the width of separation window is broadened with an increase of ionic strength. In the case of dilute suspension, the shift of i.e.p. with an increase of ionic strength was observed implying the displacement of polyelectrolytes. The morphology of flocs formed in the former is more or less rounded shape and compact structure, while under high ionic strength the morphology showed up as elongated ellipsoid like rugby football.

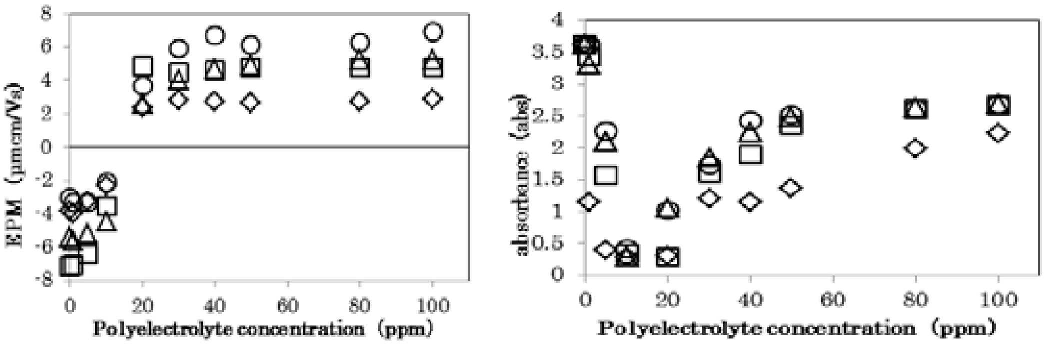

Fig.1 Absorbance of supernatant (left) and electrophoretic mobility as a function of polyelectrolyte concentration for PSL dispersion , N(0)=1.75×10^{10}cm^{-3}
○1.0×10^{-4}M KCl △1.0×10^{-3}M KCl □1.0×10^{-2}M KCl
◇1.0×10^{-1}M KCl

Tuesday

11.40 - 13.00
RABOBANK ZAAL

Effects of MF membranes deformation and permeability on filtration of clay suspension and its solution chemistry

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Emergency Events Database (EM-DAT) indicates global increase in the frequency and intensity of natural disasters from 1900 to 2013. This is due to combinations of factors: climate change phenomena and population growth in vulnerable regions. One of first priorities after disaster is to provide safe drinking water to the affected. Membrane technology offers several advantages over conventional treatment. It provides better water quality, much more compact system, more flexible, less dependent on electricity and low cost. Microfiltration (MF) membranes have been regarded as one of the oldest separation technique and used extensively for the removal of particles, turbidity and microorganisms in water treatment. However, membrane fouling and membrane deformation due to blocking and hydrostatic pressure respectively, are limiting factors in water treatment. In understanding this issue, low pressure filtration of clay suspension for water treatment purposes is investigated in this work. The effects of permeability due to variation in solution chemistry of clay suspension, and deformation due to hydrostatic pressure are the parameters studied. Clay is used as solid contaminant; one of multi-components of natural waters and hence, one of the major factors that limits the use of MF for surface water treatment because it causes membrane fouling. Clays are complex colloidal materials, thus their presence in water alter the performance of membranes due to their reactions with variations in solution chemistry as well as with water. Darcy's law could be used to explain apparent permeability change by changing the concentration of salt. This would explain the electro-viscous effects by altering zeta potential and double layers measurement, and also membrane resistance towards water. This study is important because membrane permeability control might prolong the lifetime of the membrane for water treatment. Membrane deformation is investigated by measuring pure water flux measurement prior to filtration experiment, and hysteresis phenomenon to be observed whether reversible or irreversible membrane deformation has occurred.

MODIFIED HYDROPHOBIC CERAMIC MEMBRANES: USE FOR OZONE TRANSFER TO WATER

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Membrane systems represent a relatively new and promising technology in the field of water/wastewater treatment. However, membrane fouling and the relatively high energy demands prevent the wide scale implementation of membrane processes. Chemical modification of membranes surface is a rather new and innovate idea that has drawn the interest of many researchers. The key step of membrane modification is the introduction of active groups into the surface of membrane in order to improve their performance, for example by increasing hydrophobicity, and/or to satisfy different requirements (multi-functional membranes).

In the present study, modified hydrophobic α-alumina membranes are evaluated for the transport of ozone to deionized water (mass transfer of ozone without reaction). Conventionally, ozone transfer to water to be treated is mainly carried out via injectors, bubble columns or gas diffusers. Common feature of all these techniques is the formation of bubbles; however, gas-liquid transport is a rate limiting process, depending upon the ozone bubbles diameter. Such a process almost never results to a complete ozone reaction, even when very small gas bubbles would be created; therefore, the ozone tank contactor suffers from foam problems, while an ozone destructor is usually connected to the contractor for the removal of non-reacted ozone gas. An alternative approach is the use of membrane contactors in order to optimize the contact between the gaseous and aqueous phase. Previous studies have shown that the hydrophobic membranes offer much higher efficiency of gas-liquid contact, than the hydrophilic ones. When water comes in contact to a hydrophilic membrane it penetrates into the pores, due to the capillary forces. The level of capillary pressure in hydrophilic porous media can be foreseen from theoretical approaches, as a function of pore diameters and can reach quite high values, creating problems of gas transportation. On the other hand, these problems can be overcome by the use of hydrophobic membranes. Mass transfer coefficients for the examined ceramic membranes were calculated for different operating condition such as pH, Reynolds number, temperature, etc.

Acknowledgements

The financial support through the co- Financed by the European Union and the Greek State programme EPAN-II/ ESPA: 'SYNERGASIA' Project NanoMemWater, (09SYN-42-440) is gratefully appreciated. Thanks are due also to EKETA-Laboratory of Inorganic Materials (V. Zaspalis, S.Sklari and A. Pagana) for the supplement of modified inorganic membranes.

A pneumatic micro-fluidic device for in-situ detection of mineral scaling at a membrane surface

B. Liszka[1], A.T.M. Lenferink[1],H.S Rho[3] G.-J. Witkamp[2], C. Otto[1]

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Protecting surfaces against mineral scaling poses a great challenge in water processing technology. The formed scale leads to a large decrease in membrane efficiency and large changes in surface properties and, as a result, this leads simultaneously to increasing maintenance costs. Various methods to mechanically remove scale or slow down the process of scaling have been developed. Nevertheless, much can be gained if very early stage scaling can be understood and prevented. For this reason, early scaling, under in situ conditions needs to be investigated to enable a better protection of surfaces and facilitate water quality control.

We propose here a pneumatic microfluidic device that is optically coupled with a Micro-Raman spectrometer as a method for in situ detection of sub-micron to nano-sized crystal formation on various organic membranes.

The micro-fluidic system has been prepared using standard PDMS technology in combination with masks made by photo-lithography. In order to create small, separate chambers on a chip, in which pre-nucleation and mineralization takes place, the PDMS walls are pneumatically closed. The advantage of this pneumatic micro fluidic device is that it enables control over mass transport such that experiments can be carried out in a confined volume and under well-defined conditions in solution. Additionally, Raman-based micro-spectroscopic methods like spontaneous Raman scattering and coherent Raman imaging can be applied on samples under ambient conditions in the micro-fluidic device in real time. Another aim of this work is to show that micro-fluidic devices are promising tools for studies concerning mineralization processes and will help to provide more information on underlying principles. The Raman spectra of minerals are directly informative with respect to the chemical composition and can be directly interpreted in terms of the symmetry of the crystals in case of different polymorphs. Furthermore, a great advantage is the sensitivity which is sufficient to detect nano-sized mineral particles.

Mineralization has been assumed to be highly dependent on the nature of the surface. A number of polymer materials was selected for mineralization experiments. The selected organic polymers are common in membrane technology and water filtration systems, namely polysulfone and poly(p-phenylene-oxide). Polystyrene has been added as a common material in technology. In order to observe the smallest possible nano-crystals at a polymer surface the Raman scattering of the crystals must be of the some order of magnitude as the Raman scattering from the organic layer. It was therefore decided to prepare very thin polymer films with a thickness of the order of nanometers as part of the microfluidic device.

Finally, a model super saturated mineralization solution was prepared to understand early phenomena occurring in solution. The solution was investigated by a double pulse experiment, which enables to assess the mineralization rate and gives insight in the nature of pre-nucleation prior to a mineralization process. A model mineralization solution has a well-defined metastable region which depends on parameters, such as: super- saturation ratio, pH , ionic strength, temperature.

Knowledge gathered from the double pulse experiment will help to better control in–situ detection of scaling performed by Raman imaging in microfluidics. In this way more insight may be acquired if nucleation and mineralization take place at organic surface and in dependence on the choice of the organic phase.

Momentum and mass transport over a superhydrophobic bubble mattress: the influence of interface geometry

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We numerically investigate the influence of interface geometry on momentum and mass transport on a partially slippery bubble mattress. The bubble mattress, forming a superhydrophobic substrate, consists of an array of slippery (shear-free) gas bubbles with (no-slip) solids walls in between. We consider pressure-driven laminar flow over the bubble mattress, with a solute being supplied from the gas bubbles. The results show that solute transport can be enhanced significantly due to effective slippage, compared to a fully saturated no-slip wall. The enhancement depends on the interface geometry of the bubble mattress, i.e. on the bubble size, protrusion angle, and surface porosity. In addition, we demonstrate that the mass transfer enhancement disappears below a critical bubble size. The effective slip vanishes for very small bubbles, whereby interfacial transport becomes diffusion dominated. For large bubbles, solute transport near the interface is greatly enhanced by convection.

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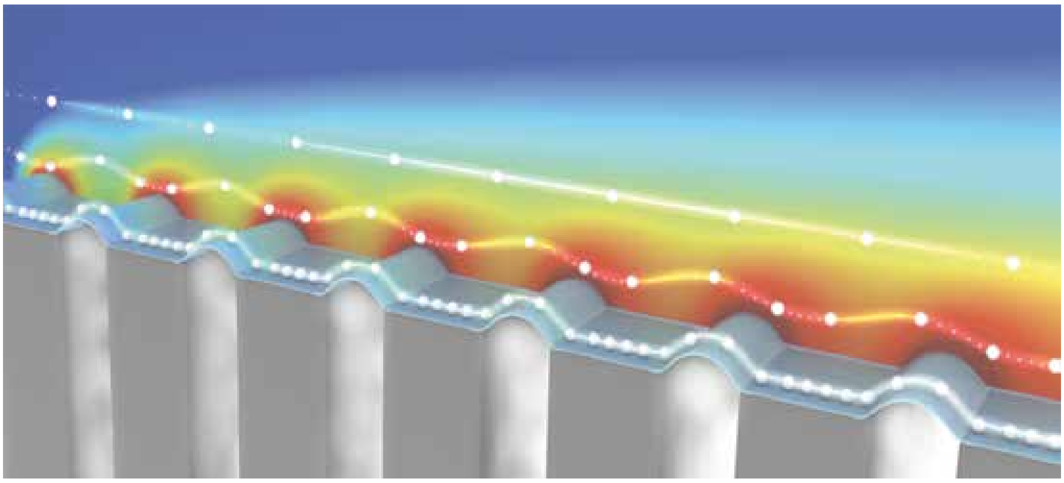

TEMPERATURE EFFECTS ON ENERGY PRODUCTION BY SALINITY EXCHANGE

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In recent years, the capacitance of the interface between charged electrodes and ionic solutions (the electrical double layer, EDL) has been increasingly investigated as a source of clean energy from salt concentration changes [1-3]. Charge is placed on the electrodes either by means of ion-exchange membranes (CDP or Capacitive energy extraction based on Donnan Potential) or of an external power source (CDLE or Capacitive energy extraction based on Double Layer Expansion). In the latter method, net energy is produced by simple solution exchange in open circuit (Fig. 1),. In this communication, we propose to explore the changes in capacitance associated to temperature variations as well: a temperature increase produced a decrease in EDL capacitance and hence a cycle is possible in which some charge is put on the electrodes at a certain potential, and returned at a higher one (Fig. 1). There is also the possibility of gaining energy from the so-called thermal membrane potential: an electric potential is generated when hot and cold waters are contacted with anion and cation exchange membranes, respectively [4]. DLE technique from the exchange of cold and warm waters (double layer permittivity exchange, DLPE) successively in contact with charged electrodes. Furthermore, we will demonstrate, both theoretically and experimentally, that temperature and salinity variations can be suitably combined (charging the electrodes in cold sea water, and discharging them in warm fresh water) to maximize the potential increase and the energy available.

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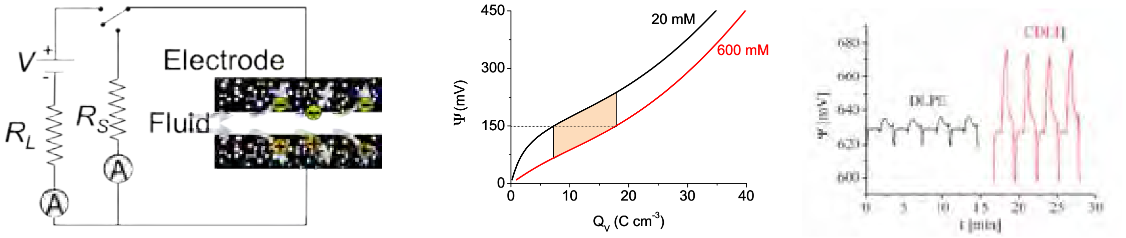

Figure 1. Left: The CDLE process; center: a typical charge-discharge cyle; right: DLPE and CDLE compared in experimental conditions. Here we demonstrate that it is feasible to gain net energy in the C

Functionalized activated carbon for “capacitive mixing” energy production

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The “capacitive mixing” (CAPMIX) technique for the energy production can be considered the reverse of CDI. In the simplest case, the so-called “capacitive double layer expansion” (CDLE) technique, we exploit the increase of the electrostatic energy of an electric double layer, that takes place when the concentration of the solution is reduced, resulting in the diffusion of the ions against the electric force. The electric double layers must be already present when the concentration is changed; they are usually generated by charging the electrodes by means of an external power supply. Now we report experiments in which the double layers are obtained by chemical means: charged functional groups are added to the surface of the activated carbon. This leads to the spontaneous formation of an electric double layer, without the need of an external device for charging the electrodes. We show that this approach leads to stable and repeatable performances of the electrodes, with a power production of the order of 100 mW per square meter of electrode.

Ultrathin metal oxide coated mesoporous carbon material for enhanced capacitive deionization

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Currently, capacitive deionization (CDI) has attracted attention as a low energy consumption and environmentally friendly desalination technique, because it can be conducted at low voltages without secondary waste. In this work we have synthesized mesoporous carbon coated with ultrathin metal oxide via atomic layer deposition (ALD) technique and used as CDI electrodes. The influence of ultrathin metal oxide on the mesoporous carbon was studied to the CDI performance. It was identified from TEM, XRD, BET and XPS that the mesoporous carbon was coated successfully by means of ALD method. As a results of cyclic voltammetry and impedance, it was identified that metal oxide coated mesoporous carbon electrode has more enhanced electric double layer capacitance and less diffusion resistance than previous carbon materials. Also charge-discharge and ion conductivity profiles showed that the ion removal ratios of metal oxide coated mesoporous carbon electrode more than that of previous carbon electrode. In conclusion, carbon electrode which was coated by ultrathin metal oxide with its high surface area and high dielectric constant shows potential for CDI electrode material more effective than previous carbon electrode in CDI system.

Mesoporous carbon nanofiber fabrication and its capacitive desalination application

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The lack of fresh water is one of the most serious problems for human beings in the 21st century. In order to generate fresh water from sea water and brackish water, various desalination methods, such as distillation, electrodialysis, reverse osmosis, activated carbon adsorption and ion exchange method have been developed for water desalting. Capacitive deionization (CDI) technology is recently becoming increasly attractive as an alternative desalination method due to low energy consumption and needless of chemicals[1-2]. CDI is referred to an electrosorption process, in which ions in water are adsorbed in the electrical double layer when electrodes are charged, and then desorbed when electrodes are discharged. At the same time, the electrode is regenerated. Because the voltage applied between the positive and negative electrodes in CDI cell is lower than that of water electrolysis(< 1.2V), water electrolysis is avoided and much energy saved[3]. Therefore, it is a very promising technology for water desalination nowadays.

The high capacitive and high conductive electrode materials are needed in order to enhance the accumulation of ions and decrease energy consumption, respectively. A high capacitive material should have a high surface area for ion accumulation. Recently, the high porous and conductive carbon based materials, such as carbon aerol gel[2], carbon nanotube[4] and carbon fiber[5] have been developed in order to increase the desalination capacity of the electrode materials.

Electrospun technique is very suitable for carbon nanofiber material fabrication with 100-500nm diameter[6]. The electrostatic force between the tip and collector electrode drives the fiber formation of a polymer solution. One of the most used polymer is polyacrylonitrile (PAN) due to its good spinnability in solution[7] and its relatively high carbon yield.[8] The resultant PAN-based carbon fiber has high surface area and tunable porous structure after suitable activation by steam activation or CO2 activation[9]. These physical activation processes were difficult to control the pore size and the porous carbon fibers were easily deactivated with recycling. In this report, we present our strategy to get the self-sustainable mesoporous electrospun carbon fiber by adding some chemicals such as polymethyl methacrylate (PMMA) or polystyrene (PS) in the electorspun polymer precursor solution as a pore-forming component. BET analysis, SEM and electrochemical characterization were made to understand the porous structure and capacitive properties. The pore size and density can be tuned by adjusting the ratio of the additives. The mesopores with 10-50 nm pore size were formed at the ratio of PAN/PMMA of 4:1. Cyclic voltammetry experiment confirmed that the specific capacitiance of the carbon fiber has a significant increase compared with the pure PAN drived carbon fiber. The capacitive desalination performance was investigated by assemblying the self-sustainable mesoporous fiber electrode in the capacitor. The salt adsorption capacitance was 6.5 mg/g and 7.5 mg/g corresponding to PAN/PS and PAN/PMMA drived carbon fiber electrode, respectively. Both are much higher than that of the pure PAN drived carbon fiber (2.3 mg/g). The stability test was measured. It demonstrates that the mesoporous carbon fiber electrode is potential for water softing and brackish water desalination application.

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CDI carbon electrode coated with ion selective layer

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Capacitive deionization (CDI) is an ion removal technology based on storing ions in the polarization layers of two oppositely charged electrodes. CDI process is defined as a potential driven adsorption of ions onto a charged electrode surface. CDI is a technology similar to that of electric double layer (EDL) super-capacitors but modified to operate in a flow through system. Conventional CDI is known to be energy inefficient because of the dissolved salt present in the pore volume of the carbon electrode. When an electric potential is applied, counter-ions in the pore adsorb onto the electrode and co-ions are expelled from the electrodes. So ion adsorption and desorption occur simultaneously in the surface of electrode, seriously reducing desalination efficiency. To solve this problem, a charge barrier should be placed near to the electrode of CDI[1]. It is called membrane-capacitive-deionization (MCDI) in which very expensive ion exchange membranes are used. So, we have developed novel CDI electrode coated with very thin ion exchange layer, which is shown in the Fig. 1. This CDI electrode leads to have very low resistance, to enhance the salt removal performance and to lower its production cost[2].

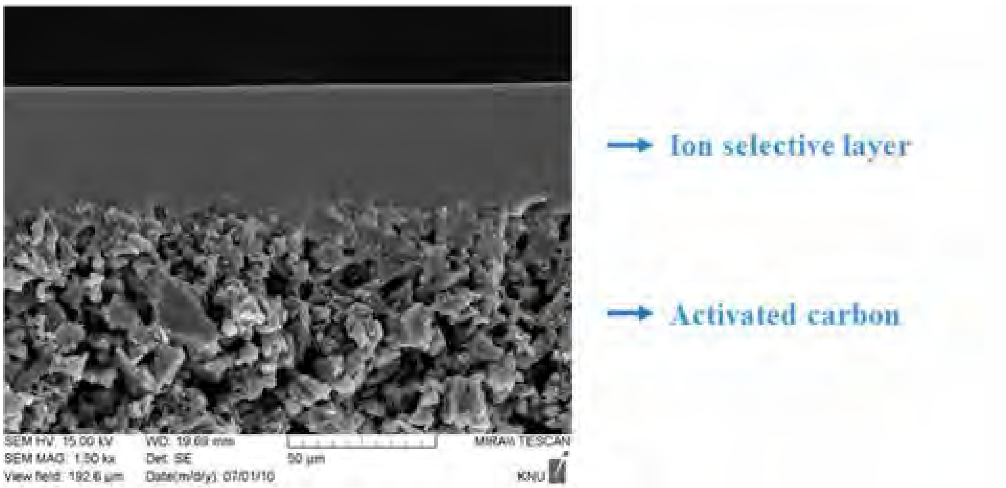

Fig. 1. SEM image of the cross section of ion selective layer coated CDI electrode.

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Keynote
Dynamics of metal uptake by biointerfaces

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In this presentation, a formalism for the dynamics of uptake of metal ions by microorganisms is discussed. The theory integrates the interplay over time between metal depletion in bulk solution, metal adsorption at the microbial interphase, metal excretion (efflux) and transport of metals by conductive diffusion toward the metal-consuming biomembrane. The model further involves basic physicochemical descriptors of the microorganism in terms of size, interfacial distribution of electrostatic charges, or thickness of peripheral soft surface appendage. A generalization of the Best equation[1] is proposed and rationalizes the evolution over time of the concentration of metal ions at the active membrane surface as a function of bulk metal concentration. Combination with metal conservation condition over the sample volume allows a full evaluation of bulk metal depletion kinetics and the accompanying time-dependent uptake and excretion fluxes as a function of metal-microorganism electrostatic interaction, microbe concentration and relevant biophysicochemical features of the interphase. Practically tractable expressions are derived in the limit where the Biotic Ligand Model (BLM) is obeyed and in situations where conductive diffusion transport of metals significantly determines the rate of biouptake. In particular, the plateau value reached at sufficiently long times by bulk metal concentration is rigorously expressed in terms of the key parameters pertaining to the adsorption process and to the kinetics of metal uptake and excretion. The theory extends and unifies previous models[2-4] where the impacts of extracellular metal transport and/or metal efflux on the overall rate of biouptake were ignored. At the end of the presentation, few elements will be provided on ongoing modelling of metal biouptake in metal-complexing media and under conditions where microbial growth kinetics contribute to the dynamic partitioning of metals across biointerphase.

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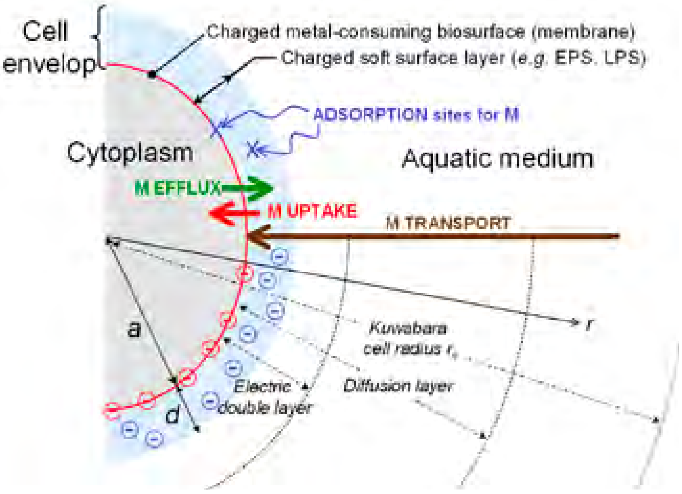

Validity of the Boltzmann equation to describe Donnan equilibrium at the Membrane-Solution Interface

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To describe Donnan equilibrium at the membrane-solution interface, the simplest approach uses the classical Boltzmann equation, based on a mean-field description of ions as ideal point charges, in combination with the assumption of fully overlapped electrical double layers in the membrane pores. We test the Boltzmann equation by measurement of the equilibrium counterion and co-ion concentration in densely charged membranes equilibrated with various NaCl solutions (0.01-3 M). To obtain a good fit of data it was found necessary to express the membrane charge and ion concentrations per volume of aqueous solution phase in the membrane, and to include a small energetic term in the Boltzmann relation. A discrepancy between theory and experiment data is found at low external NaCl concentrations. Similar deviations from the Donnan model have been reported for over half a century, but do not yet have a convincing explanation. Agreement between experiment data and theory at low external NaCl concentrations is obtained when we model the desorption experiment taking into account the role of H+ and OH- ions in closing the charge balance, and postulating the presence in the membrane of a tiny amount of fixed groups with a charge opposite to overall fixed membrane charge.

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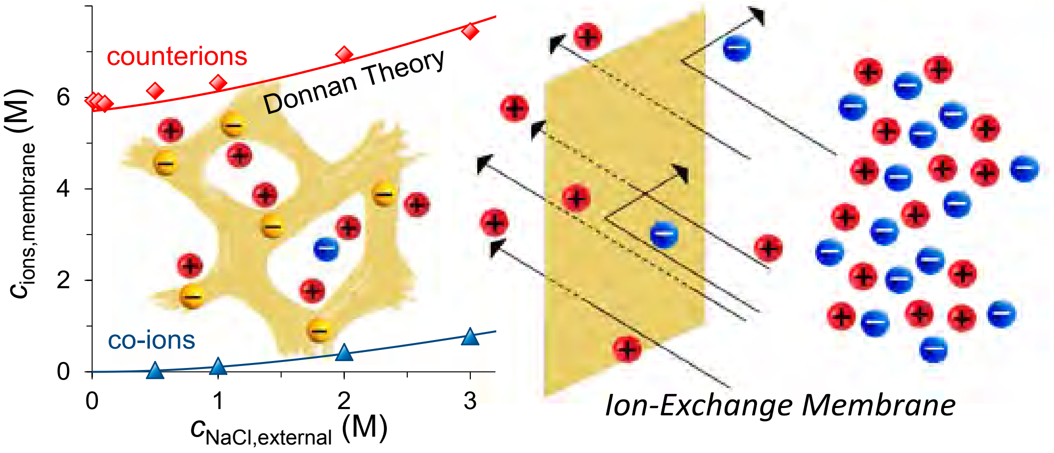

Recent advances in diffusive gradients in thin films (DGT). The role of electrostatic effects and dissolution of metal nanoparticles.

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DGT [1] is a widely used technique for measuring metal fluxes in environmental systems, especially aquatic media. In a DGT device, metal is accumulated in the beads of a resin dispersed in a gel (forming the resin layer). Metal ions arrive to the resin after crossing a diffusive layer of just gel. Metal complexes moving through the diffusive gel can penetrate into the resin layer [2,3]. This penetration of complexes into the resin layer usually enhances the accumulation, because their dissociation proceeds at maximum speed and, so, acts increasing the lability of the complexes in comparison with other sensors where the detection proceeds just in a surface (and not in a volume, like in DGT).

An adequate knowledge of the dissolution of inorganic nanoparticles (NPs) is key for understanding the environmental and toxicological impact of these materials. DGT yields an estimation of the labile fraction of metal dissolved from ZnO nanoparticles in aqueous dispersion without any prior solid/liquid separation step. The results show the relevance of pH and metal speciation in the aqueous phase on the measured labile fractions.

Electrostatic effects, due to the electrical charges of the resin beads, dramatically impact on the penetration of complexes into the resin disc. For decreasing ionic strengths, negatively charged complexes will experience stronger electrostatic repulsion from the resin layer leading to a reduction of the accumulated mass, while positively charged complexes will contribute to enhanced metal accumulations. Experimental evidences of this behaviour will be shown for Ni, Cd and Co complexes with nitrilotriacetic acid (NTA) and ethylenediamine (Etdiam). A simple electrostatic model quantitatively explains the results. By fitting the experimental accumulations, one obtains values of the Boltzmann factors which can be used in other systems. These effects are extremely important for a correct interpretation of DGT measurements in pristine waters, such as lakes [4]. Moreover, the increased kinetic dissociation constant in the resin domain (in comparison to the Eigen value in the gel domain) is an important phenomenon that supports the classical interpretation of DGT sensing mostly the labile species.

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Capacitive Response of PDMS-coated IDE Platforms Directly Exposed to Aqueous Solutions Containing Volatile Organic Compounds

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Surface-engineering of micro- and nanostructured transducer platforms with different chemical layers is gaining increasing interest for bio-medical and environmental sensing applications, including water quality monitoring. Polymer-coated interdigitated electrodes (IDEs) have shown great potential for the capacitive detection of volatile organic compounds (VOCs) not only in air, but also in water using headspace techniques [1,2]. The application of polymers with different affinities towards different VOCs onto the individual spots of an IDE multi-array allows to one to obtain a (capacitive) fingerprint of contaminated water, which can subsequently be analysed with pattern recognition tools. However, headspace technology is an *indirect* detection method as measurements are performed in the gas phase that is in equilibrium with the aqueous pollutant solution.

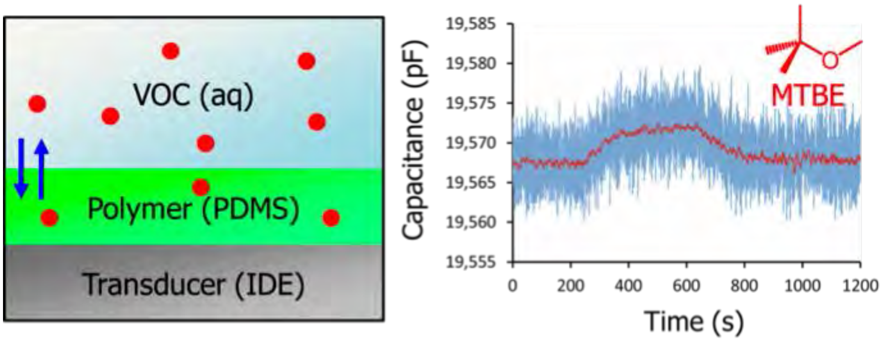

Figure 1. (left) Schematic overview of a polymer-coated IDE applied directly in water and (right) the reversible capacitive response of a PDMS-modified IDE platform to MTBE in water.

The aim of our research is to measure and understand the capacitive response of polymer-coated IDE platforms *directly* exposed to aqueous solutions containing VOCs [3,4]. Here, we present on the capacitive sensor response of polydimethyl siloxane (PDMS)-coated, micro-sized IDEs of gold when exposed to an aqueous environment spiked with different VOCs, including methyl *tert*-butyl ether (MTBE), toluene, m-xylene, benzene and n-hexane. The capacitive response changes upon absorption of the VOCs in the polymer layer are in line with their i) polymer affinity and ii) relative dielectric constants as compared to the one of thin PDMS layers. In addition, the response changes were fully reversible. Different aspects related to the application of polymer-coated IDEs directly in water as compared to gas-phase analysis will be discussed. This will include the so-called third electrode effect and the analysis of salt solutions.

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Keynote

The Importance of Carbon Electrode Material Affecting the Maximum Deionization Performance in CDI Process

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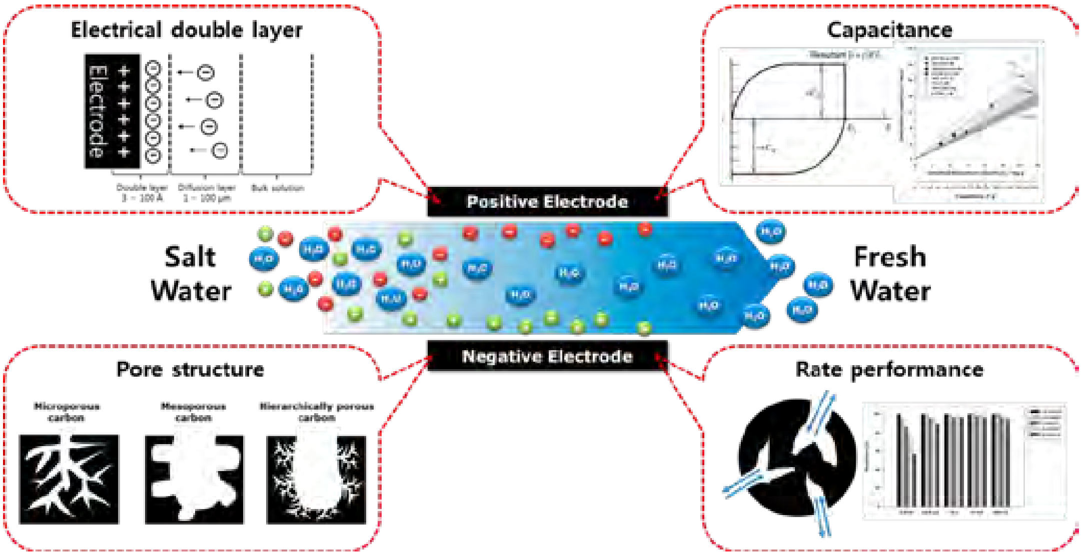
Water shortage problem is a global environmental issue today. Desalination can provide a solution to water scarcity and subsequent increasing freshwater demands in agriculture, industry, and household. Recently, capacitive deionization (CDI) has attracted growing attention as a novel desalination technology. CDI produces deionized water while saline water passes between closely-packed electrodes upon charging, in which porous carbon materials play an important role to achieve an effective desalination. Therefore, various carbon materials, such as carbon aerogel, ordered mesoporous carbon, and carbide-derived carbon, have been investigated as CDI electrodes to provide improved desalination performance. Previous studies have reported that the desalination performance in terms of deionization capacity (or salt adsorption capacity) was significantly affected by types of carbon material. In this presentation, we will show how importantly the deionization performance is affected by carbon electrode materials including their deionization capacity, especially focused on properties of carbon electrodes.



Insight into the electrochemical property of TiO_2/AC electrodes prepared by a microwave-assisted ionothermal synthesis method for capacitive deionization

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Four nanostructured anatase titanium dioxide (TiO_2)/ activated carbon (AC) composite materials for capacitive deionization electrodes were prepared by a two-step microwave-assisted ionothermal (sol-gel method in the presence of ionic liquid) synthesis method. It includes a reaction and a crystallization step. In the crystallization step, the ionic liquid plays a hydrothermal analogy role in driving the surface anatase crystallization of amorphous TiO_2 nanoparticles formed in the reaction step. The electrochemical property of these composite electrodes was investigated.

In general, the electrode prepared from the AC material with highly hydrophilic surface would have high specific capacitance. It was also reported that the specific capacitance of activated carbon electrode was enhanced after the modification of nanostructured anatase titanium dioxide. However our results found out that the effect of TiO_2 on the specific capacitance of nanostructured anatase TiO_2/ AC composite is dependent on the characteristics of pristine AC, especially for the pore size and the hydrophilicity in our study system. It may be a positive effect or negative effect. The negative effect was observed in the case of AC material with micropores and highly hydrophilic surface. These effects will be investigated and discussed using multiple techniques, including X-ray spectroscopy, thermogravimetry analysis, cyclic voltammetry, electrochemical impedance spectroscopy, etc.

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Vertically-Aligned Carbon Nanotube Electrodes for Capacitive Deionization

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We investigated the role of porous geometry using vertically-aligned carbon nanotube (VA-CNT) electrodes in capacitive deionization (CDI). CDI promises to be an efficient and compact means to achieve water desalination through adsorption of ions on high surface area electrodes. In order to optimize salt adsorption in CDI, an improved understanding of electrode properties, such as optimal pore size and electrode thickness for ion removal [1], is desired. Current studies typically use highly porous, tortuous electrode materials, which complicates the ability to obtain detailed understanding of salt adsorption and charging dynamics. In this work, we designed and synthesized VA-CNT electrodes to investigate the role of height and spacing on salt adsorption rates. The VA-CNTs were synthesized using chemical vapor deposition with inner and outer diameters of 5.6 nm and 7.7 nm, respectively, and heights of 20 to 600 µm, with specific surface areas of 540 m2/g. These VA-CNTs were transferred onto a corrosion-resistant electrode using Au-Au thermocompression bonding [2] (Figure 1). We first characterized the capacitance and charging dynamics with a three-electrode test cell in sodium chloride solution. The material capacitance ranged from 20-40 F/g in NaCl solutions of varying concentrations from 15-1000 mM, respectively. The charging time constants were extracted from the potentiostatic data (Figure 2), which indicate that the time constant varies linearly with the height of the carpet and is proportional to the Debye length. These results suggest that the charging effect is due to charge storage in the double layer and surface conduction in the CNTs. These effects may be due to the mesoporous nature of the CNT carpets. In addition, we are currently investigating the VA-CNTs in a flow through test cell, where we can correlate the results from the potentiostatic measurements to ion removal for desalination. These results offer a first step towards improved understanding of porous electrode geometries for CDI.

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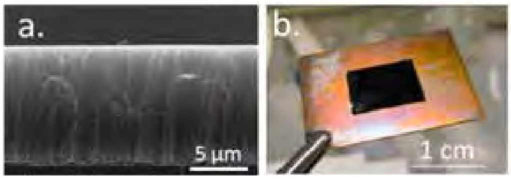

Figure 1. Synthesized VA-CNT electrodes. a) Scanning electron microscope images of transferred CNTs, b) CNT carpet transferred onto corrosion-resistant substrate.

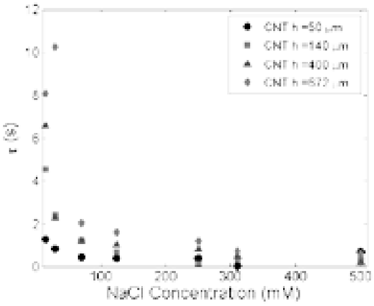

Figure 2. Charging time constant of CNT electrodes for varying heights and sodium chloride solution concentrations. Potentiostatic measurements were taken in a 3-electrode cell.

The Influence of Heteroatom Doping of Porous Carbon on the Salt Adsorption Capacity and Kinetics in Capacitive Deionization

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Key words: Porous Carbons, Salt Templating, Nitrogen-Doped, Sulfur-Doped

The production of potable, deionized water is a major challenge and capacitive deionization (CDI) has gained increased attention over the last years as an energy efficient alternative to reverse osmosis or ion exchange technologies for desalination of brackish water. Since CDI is based on the same phenomenon of ion electroadsorption as electrical double layer capacitors, porous carbons in general and activated carbons in particular are of interest and importance to CDI as they combine high surface area and low manufacturing costs with high availability. Various fabrication techniques (e.g., carbide-derived carbons, physical or chemical activation of biomass etc.) can be used to produce porous carbon materials. Especially the carbide-derived carbons are of great importance to understand the impact of the pore size distribution on the CDI process[1].

In our study , for the first time, we apply salt templated carbons for water desalination using CDI with a high surface area and pore volume derived via simple solution based bottom-up process allowing to produce porous carbons from glucose. Zinc chloride was used as a salt template to introduce porosity[2]. By careful adjusting the ZnCl2 to glucose ratio the morphology can be tuned from a microporous to a mesoporous material. The resulting carbon material can be easily doped with sulfur or nitrogen by adding soluble precursors or changing the carbon source to glucosamine. Both, the impact of these heteroatoms and the details of porosity and pore size distribution on the overall CDI performance and salt adsorption kinetics will be presented and compared with the validity of the CDI predictive tools published in Ref. [3].

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Characterization of Internal Resistance for Capacitive Deionization Systems

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Current CDI devices consume significantly more energy than the theoretical thermodynamic minimum.[1] One significant energy cost pathway is power dissipation through the internal resistance of CDI cell during charging and discharging. Therefore, understanding the contributions to resistance in CDI systems is critical for developing high performance devices. We are working to fully characterize resistive components and associated energy costs in CDI systems with the goal of reducing those resistances and developing low energy consumption devices. Internal resistance in CDI systems consists of ohmic resistance in materials, solution resistance and charge transfer resistance.[2] Figure 1 shows the resistive components in a typical CDI cell. All these components contribute to energy dissipation in charging and discharging process. We designed a custom four-probe measurement platform to measure resistivity of porous electrodes and characterize contact resistance between electrodes and current collectors under various operation conditions. We used electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge tests to perform measurements. Our characterization is based on using carbon aerogel monoliths (HCAMs)[3] as electrodes and several common carbon or metal materials as current collectors. Our preliminary results demonstrate that charge transfer resistance can be reduced by applying compression force on electrodes and current collectors (Figure 2). Other affecting parameters may include porous electrodes materials, current collector materials and feed solutions.

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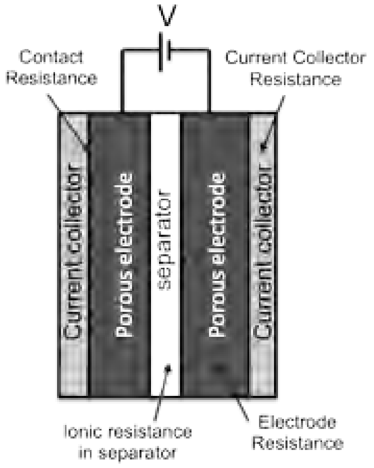

Figure 1. Resistive components in a CDI cell

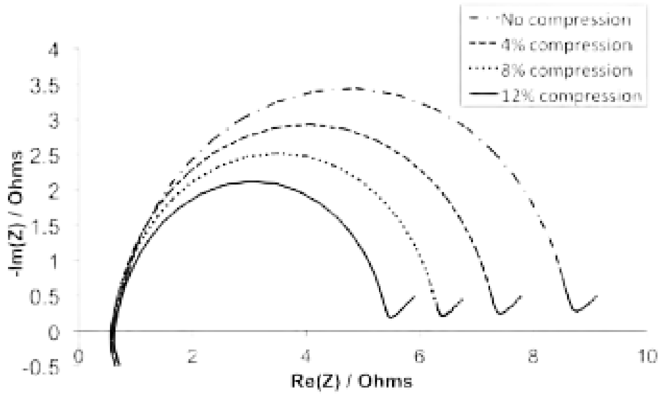

Figure 2. Reduced charge-transfer resistance by electrodes compression

16.50 - 17.50
RABOBANK ZAAL

Tuesday

Protein humic acid interaction

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In the natural environment of aqueous solutions and soil solutions proteins can form complexes with the natural dissolved organic matter. Humic acid (HA) is an important component of the dissolved organic matter. On the basis of results obtained for the humic acid (HA) - lysozyme (LSZ) system, the interactions between proteins and HA will be discussed together with their effect on the activity of the protein. In solution LSZ is positively charged and HA is negative at the investigated pH values; the discussion is relevant for other HA–protein systems when the protein is positively charged.

The charge of the HA/LSZ complexes at the IEP in the presence of KCl is compensated for 30 – 50 % by K^+; depending on pH and KCl concentration. Dynamic light scattering measurements reveal that complexation of HA with LSZ starts as soon as HA is added to LSZ and is followed by aggregation when the iso-electric-point (IEP) of the complexes is approached. Aggregation is gradual for 50 mM KCl and sudden for low KCl concentrations. The aggregate size is at its maximum at the IEP of the complexes. At mass ratios beyond the IEP the aggregates partially disaggregate. Calorimetry indicates that binding of LSZ to HA is initially enthalpically driven. Near the IEP complexation and aggregation are due to hydrophobic forces (structural re-organization) and counterion release.

The enzyme activity of LSZ decreased upon complexation with HA and the decrease of the enzyme activity increased by subsequent aggregation. A critical HA/LSZ mass ratio for the behavior of the enzyme activity was that at the IEP of the complex. Before this mass ratio was reached the LSZ activity strongly decreased under all conditions. Beyond this mass ratio both pH and ionic strength affected the activity of LSZ in the complex.

A biophysicochemical approach for assessing the dynamics of metal uptake by microorganisms

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Understanding the toxic and essential trace compounds uptake by microorganisms in the conditions that are the most relevant to the natural environment is a major trigger of concern in environmental risk assessments. One of the scientific issues is to define metal bioavailability in the vicinity of a given biological surface taking into account the dynamic interplay between physicochemical properties of pollutants, physiology of the exposed organisms, and prevailing environmental conditions. In addition, the different mechanisms involved in metal uptake (e.g. metal transport, passive and active sorption, internalization, possible excretion) may modify the metal bioavailability over the time [1,2]. In this context, the aim of this work is to develop and to propose an experimental approach able to identify the biological and physicochemical parameters controlling the metal availability and uptake by a microorganism. To this end, the time evolution of the metal depletion measured in-situ in bacteria suspension is considered as an input toward a fine mechanistic description of the biouptake dynamics. The interpretation of metal depletion kinetics in solution is supported by a theoretical approach recently developed for the description of the steady-state uptake flux of metallic ions at a charged and soft interphase of a microorganism [3,4]. The formalism provides useful information on the bio-physico-chemical processes at the bacteria-medium interphase governing metal uptake and metal bioavailability. The results that will be discussed in this presentation are obtained for two strains of soil bacteria Pseudomonas putida: one is the wild strain able to regulate metal ions and the other is devoid of efflux transporters. The time dependence of bulk metal concentration in bacteria suspension is performed with advanced electroanalytical techniques. A relevant set of metal depletion kinetic data is obtained for different volume fractions of bacteria cells. By means of the general expressions recently derived for the depletion kinetics of metal ions from bulk solution, we are able to describe the overall biouptake process dynamics and to evaluate the parameters pertaining to sorption processes and kinetics of internalisation and excretion. In forthcoming studies, our experimental approach will be extended to aquatic media containing metal-colloidal ligand mixtures.

Tuesday

16.50 - 17.50
RABOBANK ZAAL

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Sorption of organic molecules on environmental sorbents: driving water molecules in or out?

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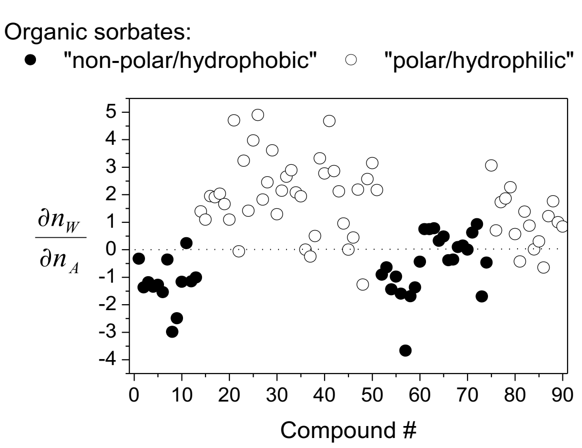
Water at inorganic and organic surfaces and interfaces is well-known to affect physico-chemical and biological reactivities of environmental sorbents, such as, e.g., soils, sediments and aerosols. In this way, water-sorbent interactions may control the environmental fate of multiple pollutants. Therefore, it is of both basic and applied interest to learn how water-sorbent interactions may be affected by the presence of sorbed organic molecules. Typically, this effect is difficult for quantification at environmentally relevant low concentrations of organic molecules. However, this quantification may be possible by considering a thermodynamic conversion of organic compound distribution coefficients K_d determined from a vapor phase (or an inert solvent medium) at variable relative humidity *RH* (or water activity) into the derivative describing the response in the sorbed amount of water molecules (n_W) to the amount of a sorbed organic compound (n_A):

$$\partial n_W / \partial n_A = \partial \ln K_d / \partial \ln RH$$

Further analysis of the relations between this differential effect and a structure of organic sorbates may be carried out by using the linear free energy relationships. In the presentation, based on the literature and own data on vapor and liquid phase sorption, this quantification is carried out for organic compounds on (*a*) various mineral phases, such as quartz, metal oxides, clays, and (*b*) natural organic matter (NOM) and humic acid, with the focus on complexed relationships between sorption of organic compounds and water molecules on NOM. The demonstration of markedly different effects of “non-polar/hydrophobic” *vs*. “polar/hydrophilic” organic sorbates on water associated with NOM is of special interest. So, sorbing hydrophobic hydrocarbons drive water out of the bulk humic acid phase whereas hydrophilic organic compounds sorbed result in an enhanced hydration of this sorbent (Figure; the effect is differentiated by the sign of the derivative). The effect of the enhanced hydration of the NOM sorbent (not observed typically on inorganic phases) may be associated with participation of several water molecules thus giving rise to “cooperativity” in water-NOM interactions, when several water molecules may (should) participate cooperatively in interactions with NOM but not in a stepwise manner. Notably, this cooperativity is induced by sorbing organic molecules. The analysis of experimental data suggests also that the NOM hydration induced and enhanced at the presence of organic sorbates may occur also when NOM (in soils and sediments) is assumed to be fully pre-hydrated by bulk water. Thus, when analyzing sorption of organic molecules from water by NOM, the continuing process of NOM hydration, at the presence of organic sorbates, may need to be included in considering the sorption mechanisms.



Vapor sorption on Leonardite humic acid
(in the 70-98% relative humidity range)

Comparison of Arsenic Adsorption on clays from Morocco

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In the recent years, growing concern for environmental issues have brought researchers of both analytical and materials science to investigate appropriate processes for the removal and/or monitoring of various pollutants. Among the pollutants, *arsenic is one* of the most toxic elements that can be found, as it is a strong poison and a carcinogen. Unfortunately, it is released into the environment during many industrial processes. Thus, *the removal of arsenic* from process solutions and effluents is necessary to protect the environment.

The aim of this work is to study arsenic adsorption behavior onto clays from Morocco. Four clay samples were investigated: red clay and yellow clay from Oued aou (Tétouan), E clay from Tetouan and stevensite from the south-eastern border of the Tertiary basin of Missour.

Adsorption isotherms were conducted as a function of pH, and initial As concentration. Also the kinetics of adsorption was investigated and FTIR, CEC, TOC, XRD measurements were performed on red and yellow clays.

The effect of the pH on the adsorption of As for the 4 clays is shown in figure 1. From this result, arsenic adsorption was most favorable in acid medium for red clay, yellow clay, and E clay. For stevensite, no significant adsorption was found in the whole pH range considered.

The kinetics experiments of adsorption of arsenic on the four clays were found to be comparable to a pseudo-second –order model.

Langmuir and Freundlich isotherms were employed to describe the Arsenic adsorption in this clay. The result obtained shown that these two models are favorable process of red clay and E clay. Furthermore, for yellow clay and stevensite were correlated by the Langmuir and Freundlich models respectively.

The order of affinity of As toward the 4 clays was red clay> E clay> stevensite > yellow clay. This order of affinity is explained by the presence of iron oxides (hematite) revealed by IR analysis of the solid in the red clay. On the other hand, neither CEC nor TOC data allowed us to conclude about this order of affinity.

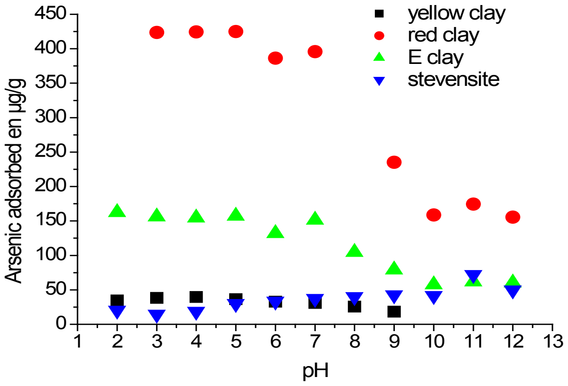

Figure 1: Effect of pH on the adsorption of Arsenic

Attenuation of metal cations by iron oxide minerals from acid mine drainage

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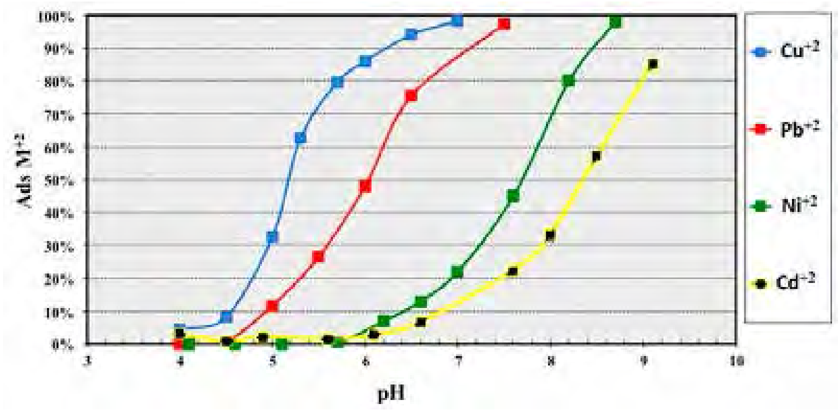
The formation of acid mine drainage (AMD) implies the weathering and oxidation of the iron sulphide minerals present in mining areas and the formation of large amounts of secondary iron precipitates. The presence of these secondary iron precipitates can be considered of great importance, since they are naturally occurring scavengers for most of the contaminants that acumulate in these areas and their presence controls its mobility and availability. Since sorption is one of the best methods for the removal of contaminants, natural aluminium and iron oxides from AMD are the main responsibles for the speciation and fate of heavy metals and other species commonly found in mining areas to prevent its leaching through the soil profile and the contamination of ground and surface waters.

In the present study we have precipitated iron oxides from water samples collected at two different points of the Touro abandoned copper mine (Iberian Piritic Belt, Galicia, NW Spain). The precipitates were characterized and the XRD and SEM images showed that they looked very much like schwertmannite. The retention of Cu, Cd, Ni and Pb on these AMD precipitates was analyzed under different experimental conditions (different pH) and the affinity series found was: Cu > Pb > Ni > Cd (see figure).

Also, the ageing of the precipitates was conducted during 1 and 6 months at the original pH of the AMD water samples (pH ~ 3). It was found that depending on the origin of the sample and the ageing time, the precipitate can undergo a transformation from an amorphous swertmannite–like form to a crystalline goethite–like form. The different retention of the same heavy metals previously studied cofirmed the transformation process sufered by the iron oxides. In an attempt to model heavy metals retention in these natural iron oxides analogous to some sinthetic oxides, surface complexation models have been applied.



Adsorption and aerobic biodegradation of three selected endocrine disrupting chemicals in artificial groundwater recharge with treated reclaimed municipal wastewater through river utilization

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EDCs (endocrine disrupting chemicals) pollution in river-based artificial groundwater recharge using reclaimed municipal wastewater poses a potential threat to groundwater drinking water supplies in Beijing, China. Laboratory leaching column experiments simulating recharge were conducted to study adsorption, aerobic biodegradation, transport and leaching characteristics of three selected EDCs 17β-estradiolum(E2), ethinylestradiol(EE2) and bisphenol A(BPA). Representative soil vadose zone media from the ChaoBai River were used as filler for the three columns. The three columns were operated in the condition of continual sterilization recharge, continual recharge and wetting and drying alternative recharge. The results showed that the attenuation of EDCs was in the order of E2 > EE2 > BPA, which followed the principle of first-order kinetics. The EDCs decay rate constants were 5.6 m^{-1}, 5.2 m^{-1} and 4.7 m^{-1} for E2, EE2 and BPA in continual recharge system, respectively. The adsorption ratios of the soil were 98%, 96% and 92%. While, the biodegradation ratios were 1.1%, 1.7% and 4.2%. The EDCs decay mainly depended on soil adsorption with depth. The EDCs attenuation by unit mass was 1.685mg $(100g)^{-1}$, 1.032 mg $(100g)^{-1}$and 0.172 mg $(100g)^{-1}$, respectively. The inflection points of EDCs concentration at different depths were 0.3m. In one column system with wetting and drying alternative, the concentrations of EDCs dropped 0.2%, 1.2% and 2.3% than the continual recharge system. The EDCs biodegradation was affected by water temperature; when the temperature was below 5 °C, the conversion of EDCs did not change significantly with depth and time. The adsorption capacity decreased 8%, 7% and 13% when the temperature increased from 20 °C to 40 °C. Groundwater EDCs pollution was related to the adsorption and degradation capacity of the soil vadose zone media. To avoid or minimize possible EDCs contamination of groundwater in artificial groundwater recharge areas, the amount of EDCs in treated reclaimed municipal wastewater has to be determined and minimized by optimizing reclaimed water treatments, optimizing the management of the recharging operation and enhancing the ecological purification function of rivers.

Study of Electrosorption Performance of Nanostructured Carbon Electrodes in Capacitive Deionization

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Capacitive deionization (CDI), or referred to as electrosorption process, is a promising nanotechnology as a means of saving energy and producing purified water. The working principle of CDI relies on electrochemical separation of ions onto highly porous carbons, which is similar to that of energy storage in supercapacitors. It is noted that the choice of nanostructured carbon electrodes is the key factor to determine the deionization performance. The objective of this study is to identify the effect of pore characteristics on desalting capability in the CDI process. Several carbon materials with various porosities, such as carbon aerogel, activated carbon, multiwalled activated carbon, and ordered mesoporous carbon, are tested. The capacitive behaviors of carbon electrodes are evaluated by using cyclic voltammetry. Electrosorption experiments with a CDI cell are carried out to assess the deionization performance of carbon electrodes. The obtained results show clear trends in the relationship between the electric double-layer capacitance and electrosorption capacity. Also, the carbon materials possessing the different pore sizes show different types of cyclic voltammograms. One can see that the electrosorption capacity strongly depends on the specific surface area and the pore size distribution of carbon materials themselves. The carbon electrodes associated with larger mesoporosity result in a higher effective surface area and greater electrosorption capacity. The good electrosorption performance could be attributed to the presence of mesopores that are less affected by double-layer overlapping and then facilitate ion transport in the CDI process. More specifically, Grand Monte Carlo simulations (GCMC) can be further used to provide the insights into ion distribution inside charged nanopores and to predict its electrosorption capacity. The findings of this work can provide useful information to search the desirable carbon materials in CDI process.

Pore-structure of Activated Carbon Fibers on Capacitive Deionization

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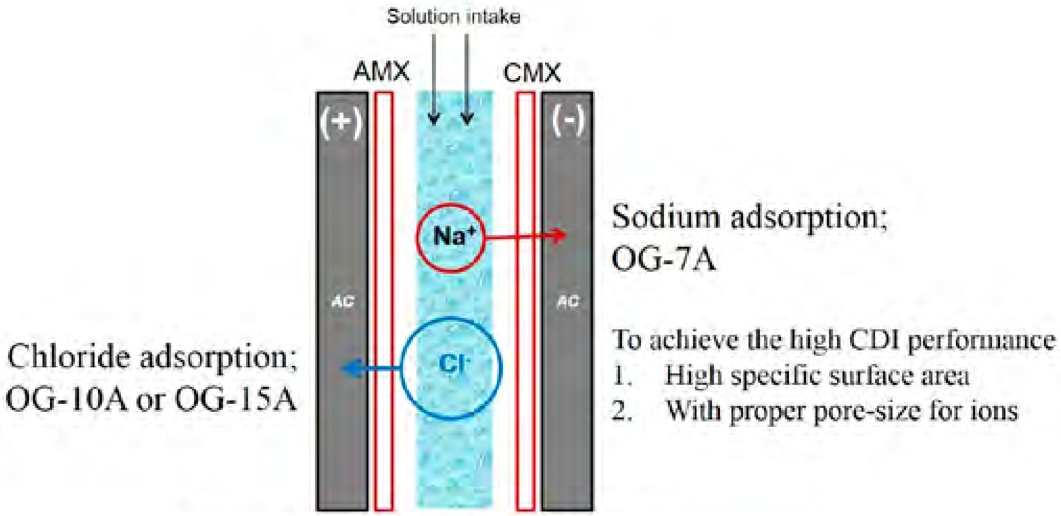
We develop the capacitive deionization (CDI) system for the purification of sodium-chloride containing water using activated carbon fibers. The pitch-based activated carbon fibers (OG-series; 7A, 10A, 15A, 20A from Osaka gas Co. Ltd. Japan) have varying degree of activation with different surface area and pore-distribution. These materials were applied in CDI system and evaluated the ion adsorption capacity of sodium/chloride respectively. The experiments were conducted at various applied voltage, solution feed rate, and concentration. The results of experiments indicate that the pore structure of OG-7A is suitable for sodium ion adsorption and OG-10A or OG-15A has adequate pores for chloride. The detailed relations between the desalination of sodium/chloride ions and pore-structure of activated carbon fiber are discussed in this presentation.



To achieve the high CDI performance

1. High specific surface area
2. With proper pore-size for ions

	$a_{s_{BET}}$/m^{2}g^{-1}	Wp,peak(volume)/nm	Wp,peak(area)/nm
OG-7A	**861**	**0.6911**	**0.6911**
OG-10A	**1228**	**1.3036**	**1.0852**
OG-15A	**1793**	**1.5220**	**1.3036**

Capacitive Deionization with PZC-Modified Carbon Xerogel: Half-Cell and System Analysis for Long-Term Operation

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Capacitive deionization (CDI) is an emerging water treatment technology that holds many benefits over existing pressurized membrane separation systems including low energy cost of separation, modular design, and possibly lower capital and maintenance costs.(1) This growing technology has not become commercially widespread for a few reasons:

1 Cost competitive carbon electrodes capable of higher salt capacities are still needed
2 Demonstration of longer equipment lifetime needs to be accomplished
3 Energy benefits of the operation need to be further shown and compared to existing reverse osmosis (RO) systems and other combined water treatment technologies
4 Marketing the technology needs to take place to interested customers in a variety of markets

In recent years, CDI has come a long way towards meeting these goals, especially with the inclusion of membranes which are capable of not only increasing the salt capacity of the electrodes, but also of enabling fast regeneration of the adsorption surface.(2, 3) While the addition of membranes is quite attractive, it comes at the cost of added complexity and the increased possibility for fouling.

An alternative to membrane capacitive deionization (MCDI) is the use of a potential of zero charge (PZC) modified carbon electrode that can increase the salt capacity of the electrode while also possibly decreasing the overall costs of the device.(4-6) These cost effective PZC-modified carbons can increase charge efficiencies by up to 50%.(7) However, the functional groups on the carbon surface will change over time as Faradaic oxidation reactions occur. These new oxide groups can substantially affect the salt capacity of the carbon electrodes and must be dealt with to maintain the separation ability of the CDI process. In the work presented here, various mitigation mechanisms will be shown that can extend the lifetime of a CDI cell by controlling the surface oxide groups and limiting the shifting of the PZC into regions that can negatively affect the electrosorption capacity and charge efficiency. Both chemical and electrochemical options will be demonstrated with cycling experiments carried out at greater than 150 cycles.

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ORAL PRESENTATIONS WEDNESDAY

DIFFUSION OF ANTHROPOGENIC ORGANIC MATTER IN CLAY ROCK

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Small organic molecules are present in natural soils, sedimentary rocks, but also in mixed radioactive or hazardous wastes. Some organics are released by wastes and these co-contaminants potentially affect the migration of cations. The sorption of organic compounds in soils is largely studied [1], but the quantification of organics diffusion parameters is less common because of time consuming experiments. In this work, we focused on transfer parameters in clayrock of anthropogenic organics which are found to be relevant in the field of radionuclide migration. Results are discussed with emphasis on diffusive behaviour and effects on cations and complexes mobility. The Callovo-Oxfordian clayrock (COx) is investigated by the French radioactive waste management agency (ANDRA) in the context of the underground retrievable nuclear waste repository project (Cigéo). There is already a large dataset on ions diffusion in COx clayrock [2,3]. Recent results obtained on isosaccharinate, EDTA, oxalate and phthalate will be presented. The sorption isotherms, hysteresis and diffusion parameters have been quantified using 14C-radiolabelled tracers. The effective diffusion coefficient, De, of organic species is mainly driven by anionic exclusion and size effects, whereas diffusion of cations is mostly affected by hydration and surface effects (Figure 1). Diffusion experiments still confirmed a low sorption of organics on clayrock.

In a second part, we focused on europium sorption in presence of organic molecules. The sorption of europium at low organic concentration is reversible and almost independent of the presence of ligands. A decrease of europium sorption appears with the formation of anionic complexes. At high concentration of organics, the solid/solution distribution ratio, Rd(Eu), reaches a plateau and displays a strong hysteresis. This result may indicate a sorption mechanism with ligands acting as a bridge between mineral surfaces and europium and possibly a modification of the sorbing phase. Other experiments are necessary to confirm these hypotheses and to determine which solid phases are involved. The characterization of such a behaviour was useful for assessing the relevant species, concentrations and effects of anthropogenic organic in the field of deep geological nuclear waste storage.

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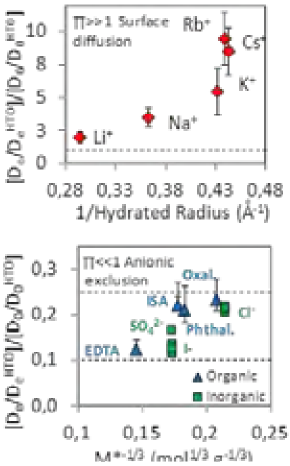

Figure 1. Diffusivity in COx clayrock : $\Pi=[D_e/D_e(HTO)]/[D_0/D_0(HTO)]$. Values for alkaline cations (Top, [2]) and various anions (Bottom, [3,4]).

Uranium migration at nuclear waste management facilities: experimental versus thermodynamic modeling

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Uranium is a common aquifer contaminant of concern at nuclear waste management facilities around the world. The most significant pathway for uranium migration is via groundwater transported away from such sites. Uranium mobility in oxic groundwater is believed to be controlled by adsorption of U(VI) on mineral surfaces of iron oxides and clay minerals due to their high sorptive capacities and common occurrence. Liquid radioactive wastes of the Angarsk Electrolysis Chemical Complex AEC (Irkutsk region, Russia) and of the Electrochemical Plant ECP (Zelenogorsk, Krasnoyarsk region, Russia), which have produced enriched uranium since 1960s, are formed during neutralization of nitric slurry after the U extraction by hydrated lime. A significant part of the residual U precipitates as poorly soluble calcium uranates or during the crystallization of calcite and other Ca-phases in the sludge ponds. One of the outstanding tasks in the study of (co)precipitation is the investigation of pH effect and carbonation of those waste disposal systems, in which high pH-values are established. The results of detailed sampling of groundwater and surface water near the storage sites of radioactive waste are presented elsewhere (Gaskova, Boguslavsky, 2013). The purpose of this investigation is to describe the results of dynamic experiments of the waste materials leaching by artificial groundwater and of the U sorption with two types of clay wall-rock sample as a function of rock:water ratio. Different thermodynamic models have been employed to elucidate uranyl sorption onto Fe-oxides, clay and carbonate minerals to explain the mechanisms controlling the uranium uptake. Thermodynamic modeling at 25°C and 1 bar total pressure was performed with the "HCh" code using a free energy minimization algorithm (Shvarov, 2008). We modeled the heterophase 13-component system H-O-Ca-Si-Al-Fe-Mg-K-S-N-C-F-U system; the solid, dissolved and adsorbed U-species were incorporated into the model using data from the literature. Table 1 and Fig. 1 is an example of interrelated experimental and thermodynamic modeling results.

Table 1. Mineral composition, conditions and results of dynamic experiments during 80 days

Angarsk ECC waste	Zelenogorsk ECP waste
CaF_2, $CaSO_4$*$2H_2O$, $Mg(OH)_2$, $CaCO_3$, trace of Quartz, $CaAl_2(CO_3)_2(OH)_4$*$6H_2O$, Ettringite, Voltaite, Fe- and Al-oxides, Illite-smectite. Micron-sized isolation of U-Ca-phases. Total U content is ~0.2%.	$CaCO_3$, $CaSO_4$*$2H_2O$, Ettringite, minor Quartz (5-10%), Fe (hydro)oxides, CaF_2, trace of $NaAl(SO_4)_2$*$12H_2O$, $CaSO_4$*$0.5H_2O$, $Ca_2(CO_3)SO_44H_2O$ and Chlorite. U-minerals were not detected. Total U content is ~0.01%.
Weight leaching of solid sample (%), mineralization of solution (mSm/cm) and final U concentration (mg/L)	
6%, 0.35 mSm/cm, nearly constant 0.23 mg/L	39%, 1.8 – 0.4 mSm/cm, nearly constant 0.002 mg/L
The percentage of solid U extracted by the CH3COONH4 + HNO3 solution (connected in the carbonate fraction)	
82%	93%

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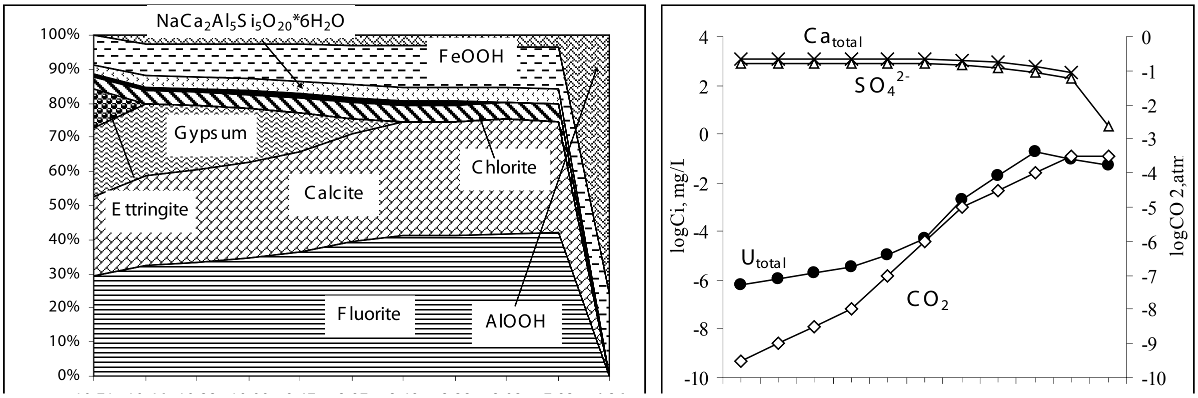

Fig. 1. Modeling data for U-containing sludge dissolution showing both (left) percentage of minerals and (right) solution composition versus pH at different pCO2,atm.

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Acknowledgements

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Adsorption of sodium dodecylbenzene sulfonate in highly humic volcanic ash soil

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Sodium dodecylbenzene sulfonate (DBS) is a very useful and widely used anionic surfactant. This surfactant sometimes creates environmental problems when it is released into the environment. However, the factors influencing the adsorption of DBS in soil have not been studied well. In this study, the influence of the potential at the adsorption site on the adsorption of DBS in a soil was first elucidated by using a theoretical adsorption equation. The soil was a highly humic soil with a negative charge. The amount of DBS adsorbed was measured with a batch method for different electrolyte concentrations of NaCl at pH 4.5 and 6.5. The adsorption site potential of the soil was obtained with the modified Langmuir adsorption equation. The adsorption of DBS decreased as the electrolyte concentration decreased and as the pH increased because the repulsive electric potential between DBS and the soil increased. These results were confirmed by the obtained adsorption site potential and the measured zeta potential. The difference between the adsorption of DBS with a linear and with a branched carbon chain was also detected, and this difference was related to the free energy of micellization. Because DBS adsorption is strongly affected by electrolyte concentration and pH, these two factors must be carefully considered to predict the fate of DBS in environmental applications.

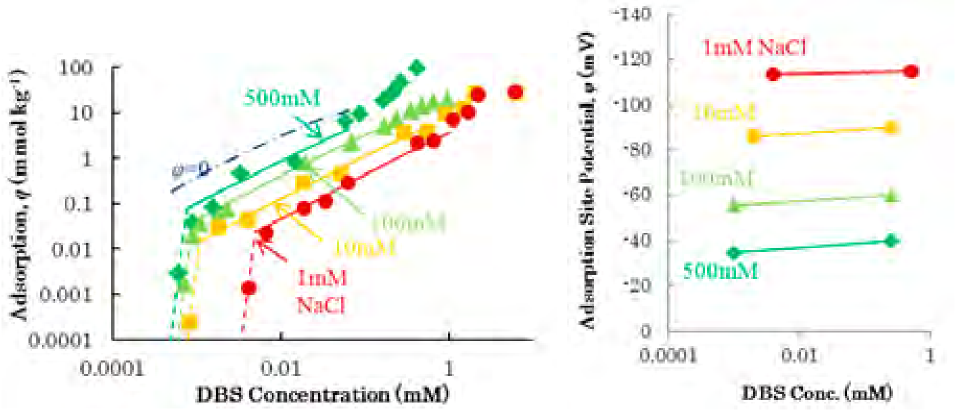

Fig. 1 Influence of electrolyte concentration and adsorption site potential on DBS adsorption isotherm.

Coupled Effects of Hydrodynamic and Solution Chemistry Conditions on Long-Term Nanoparticle Transport and Deposition in Saturated Porous Media

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This study aims to systematically explore the coupled effects of hydrodynamic and solution chemistry conditions on the long-term transport and deposition kinetics of nanoparticles (NPs) in saturated porous media. Column transport experiments were carried out at various solution ionic strengths (IS), ion types (monovalent and divalent), and flow velocities utilizing negatively charged carboxyl-modified latex NPs of two different sizes (50 and 100 nm) using acid washed medium sized river sand. Most experimental studies of NP deposition in porous media have focused on the initial clean bed deposition. In this study the experiments were designed to obtain the long-term breakthrough curves (BTCs) in order to unambiguously determine the full deposition kinetics and the fraction of the solid surface area (S_f) that was available for NP deposition. The experimental evidence accessible in the literature on the dependency of S_f on physiochemical and hydrodynamics factors, especially for NP are very narrow. The BTCs exhibited a bimodal shape with increasing solution IS; e.g., BTCs were initially delayed, then they rapidly increased, and then slowly approached the influent particle concentration. Most research were conducted in the presence of monovalent electrolyte. In this study we compared the effect of monovalent (NaCl) and divalent ($CaCl_2$) solution chemistry. NP deposition was much more prominent in the presence of Ca^{2+} than Na^+ at any given solution IS. Deposition dynamics of NPs was successfully simulated using a two-site kinetic model that accounted for irreversible deposition and blocking (e.g., a decreasing deposition rate as the available site filled) on each site. Results showed that S_f values were controlled by the coupled effects of flow velocity, solution chemistry, and particle size. Data analyses further demonstrated that only a small fraction of solid surface area contributed in NP deposition even at the highest IS (60 mM NaCl and 3mM $CaCl_2$) and lowest flow velocity (1 m/day) tested. Consistent with previous studies conducted with clean sand, our results imply that NP deposition occurred because of physicochemical interactions between the negatively charged COOH groups on the NPs and nanoscale physical and/or chemical heterogeneities on the sand surfaces that produced localized nanoscale favorable sites. Furthermore, our results suggest that the NP interactions with the collector surfaces tended to strengthen with increasing contact time.

Coverage and disruption of phospholipid membranes by oxide nanoparticles

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The interaction between nanoparticles and biological membranes has been subject of much research over the past decades, mainly for two reasons. On the one hand, engineered nanoparticles are used in many products, for example cosmetics, tires, coatings and anti-bacterial substances. Since a large part of these particles ends up in the environment, concerns have raised with respect to their possible (cyto)toxicity. On the other hand, nanoparticles may be used as vehicles for drug delivery into cells. In both cases an important question is whether they can enter a living cell, i.e., how do they interact with the cell membrane and can they cross it?

In our studies we focus on the interaction of oxide nanoparticles, in particular silica and titanium dioxide with phospholipid membranes. We show how electrostatics plays an important role in this interaction. For this we systematically varied the charge density of both the lipid membranes by changing their composition, and the oxide particles by changing the pH. Results from our fluorescence vesicle leakage assay [1] are combined with recent data on particle adsorption onto supported lipid bilayers obtained by optical reflectometry and AFM imaging. Self-consistent field (SCF) modelling [2] has been applied to interpret the results on a molecular level.

At low particle charge density no barrier for adsorption exists and the adsorption rate is determined by transport kinetics only. Both the adsorption rate and adsorbed amounts drop with increasing (negative) charge densities on particles and membranes (see e.g. Figure 1) due to electric double layer repulsion. This is confirmed by the effect of the ionic strength. SCF calculations show that charged nanoparticles change the structure and dynamics of lipid bilayers by a reorientation of the zwitterionic phosphatidylcholine (PC) head groups. This explains the affinity of the silica particles for PC lipid layers, even at relatively high particle charge densities.

Particle adsorption does not always lead to disruption of the membrane integrity as is clear from comparison of the leakage and adsorption data. Using AFM we can distinguish between particles that penetrated into the bilayer and particles that resided on top of the bilayer, depending on physicochemical conditions. Our results may be extrapolated to a broader range of oxide nanoparticles and ultimately be used for establishing more accurate nanoparticle toxicity assessments.

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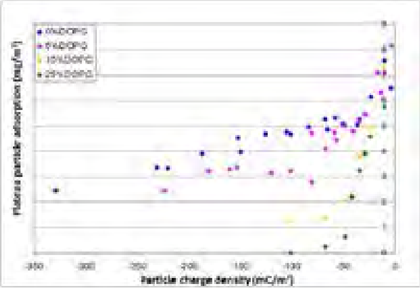

Figure 1. Adsorbed amounts of silica particles on supported lipid membranes as a function of particle charge density. The (negative) charge on the membranes increases with DOPG (a negatively charge phospholipid) content.

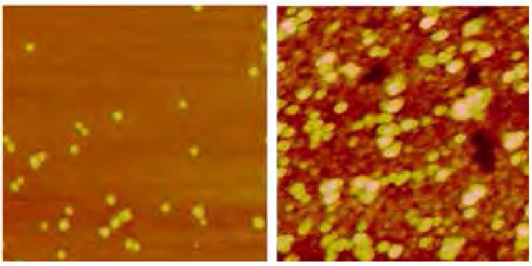

Figure 2. AFM images of silica particles (diameter 15 nm) on uncharged DOPC membranes adsorbed at pH 10.6 (left) and pH 6.0 (right). The particle charge densities were around –0.33 C/m2 and –0.01 C/m2, respectively.

Wednesday

9.20 - 10.40
NIVO NOORD ZALEN

Shape evolution synthesis of crystalline hematite (α-Fe_2O_3) nanoparticles using ascorbic acid and tartaric acid

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Iron oxides and hydroxides 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 hematite can be promoted by employing Fe(II). However, Fe(II) is an unstable reductant that can be oxidized easily when exposed to air. Organic ligands where Fe(II) is produced in the reaction mixture instead of added could avoid this disadvantage. These ligands adsorb to the ferrihydrite and serve as electron channel during the reduction of Fe(III) of ferrihydrite to Fe(II). Ascorbic acid (AA) and tartaric acid, which are widely present in nature, are good candidates for the reduction of Fe(III) to Fe(II) as electron donor.

Ascorbic acid instead of Fe(II) effectively catalyzes the formation of α-Fe_2O_3 and the particle morphologies are successfully controlled by the amount of ascorbic acid for the first time. Spherical, ellipsoidal and elongated hematite particles have been obtained (Fig. 1). Various shapes of the prepared α-Fe_2O_3 on catalyzed degradation of methylene blue are substantially different. The elongated particles that had the highest specific surface area were most effective.

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 control morphology of hematite. The products were corn-like at initial pH 7 through oriented attachment (Fig. 2), but changed to be round by ostwald ripening mechanism at high pH (pH=11).

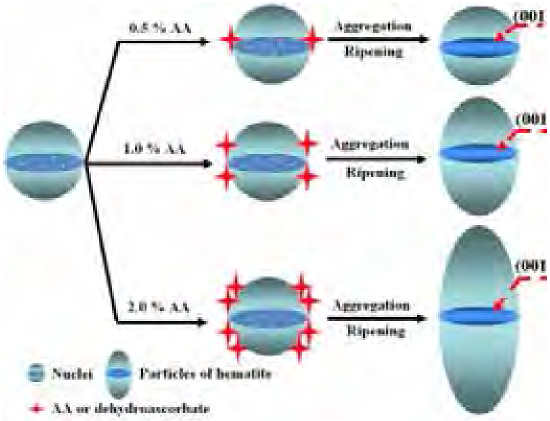

Fig. 1 Schematic illustration of the shape development of hematite synthesized at different AA/Fe(III) ratios

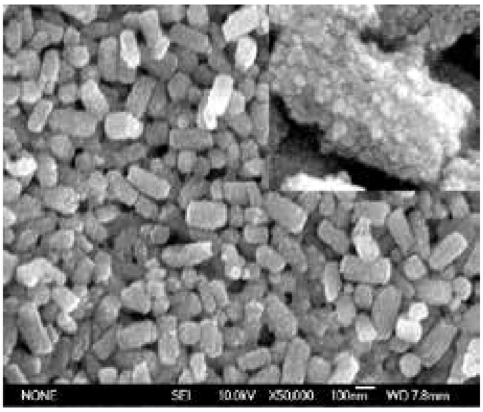

Fig. 2 SEM images of hematite synthetized at pH 7

Removal of organic pollutants from water by TiO_2/C_nTAB Nanoskeleton

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Adsorption is considered as one of the effective and versatile methods for removal of the chemical contaminants from wastewater. Thus, the development of absorbents is an important and challenging task for environmental remediation. In recent years, the combination of titanium dioxide (TiO_2) with organic/inorganic hybrid porous materials such as organic molecules-grafted mesoporous materials and surfactant-templated mesoporous materials have attracted attention because organic domains in the mesoporous inorganic materials interact with organic pollutants and TiO_2 degrades the organic pollutants adsorbed on the mesoporous materials due to the photocatalysis. Then, in this work, we develop the hybrid particles of TiO_2 and surfactant, and examine the potential of the hybrid particles as both adsorbent and photocatalyst for removal of organic pollutants from water. The hybrid particles (named as TiO_2/C_nTAB Nanoskeleton) was prepared through the so-gel reaction of titanium oxysulfate sulfuric acid hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) initiated by alkyltrimethylammonium bromide ($C_nH_{2n+1}N(CH_3)_3Br$, C_nTAB; n = 12, 14, 16 and 18) micelles in an aqueous solution at 60 ˚C for 24 h. The TiO_2/C_nTAB Nanoskeleton is a hexagonal-structured assembly of nanocrystalline anatase TiO_2 and C_nTAB. We found that alkylphenols dissolved in water were removed through the adsorption of alkylphenols onto TiO_2/C_nTAB Nanoskeleton. On the other hand, no significant adsorption of alkylphenols onto TiO_2 Nanoskeleton (that was obtained after calcination of TiO_2/C_nTAB Nanoskeleton) was observed. This indicates that the adsorption of alkylphenols onto the TiO_2/C_nTAB Nanoskeleton is attributed to the hydrophobic interaction between alkylphenols and C_nTAB domains. We also found that alkylphenols dissolved in water was completely removed by the combination of adsorption and photocatalysis of TiO_2/C_nTAB Nanoskeleton under UV irradiation. This proves that the TiO_2/C_nTAB Nanoskeleton acts as in tandem an adsorbent and a photocatalyst for removal of organic pollutants dissolved in water.

Wednesday

9.20 - 10.40
NIVO NOORD ZALEN

Smart Hybrid Nano-Composite Devices for Removal of PAH Micro-pollutant from Wastewaters

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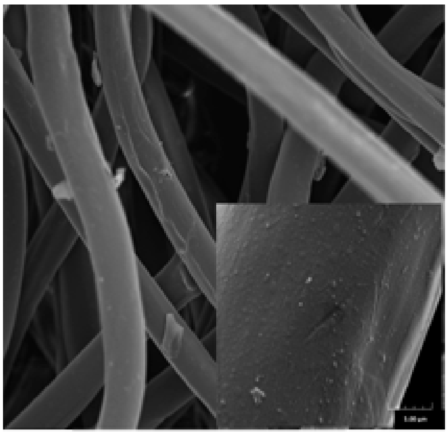
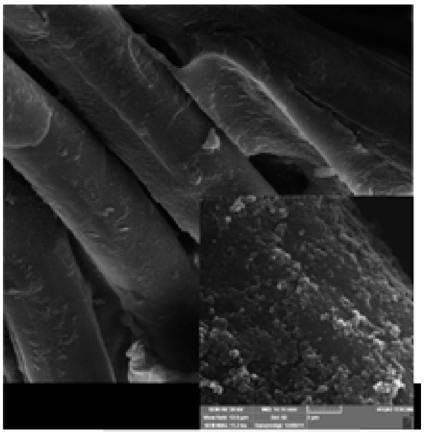
Natural and drinking water supplies are being increasingly contaminated with emerging organic micro- (diluted-) pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs), which have been identified as carcinogenic and are non-degradable. Absorption is considered to be a very effective method of quick lowering of the concentration of dissolved pollutant in an effluent. However, traditional treatment using membrane or activated carbons have some limitations such as fouling and weak sorption ability due to their weak interaction with the target contaminants or difficulties to be regenerated respectively and, hence, require a radical change in the fundamental structure of the substrates.

This presentation will address a new concept in efficient nano-sorbent for the sustainable removals of PAH micro-pollutant from wastewaters. The technology is based on the conception of novel nano-composite materials consisting of technical textile fibers functionalized by Organic/Inorganic nano-coatings (see figure below). We will discuss results from synthesis and characterizations of new molecular precursors for the Sol-Gel process to the remarkable advantages of the resultant hierarchical micro-, nano-structured nano-composites, giving low cost and strong mechanical structures that can withstand high water flow rate for long time (a prerequisite. We will also demonstrate the relationships between the mode of coordination, the nature of the trapping sites of the ligand (pi-stacking) and high removal capacities and selectivities, fast adsorption rates and recycling properties for PAH organic moieties.



Textile before grafting



Grafted textile

Temperature effects on the desalination of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigated the effect that varying the temperature of the water has on the properties of blue engine and desalination cycles. Desalination cycles were found to be most effective when cold water is used. There is a ~10% decrease in required energy when changing from equatorial to arctic sea water.

Furthermore, we studied the effect of using water at different temperatures within one cycle. Saline water reservoirs at different temperatures can be obtained by e.g. pumping sea water from depths to the surface or by using cooling water from industrial facilities in an intelligent way. Desalination becomes increasingly cheap when performing the charging step in sea water of lower temperature than the discharging step. Interestingly, the characteristics of the engine (pore size, pore volume, bath volume) can be tailored such that the required energy vanishes already for small temperature differences.

These positive temperature effects on the efficiency are not at all exclusive to desalination cycles, similar temperature effects are also observed in blue energy cycles. We find that blue energy harvesting can be enhanced when fresh water is used which has a higher temperature than the sea water. For large temperature differences of the order of 50 degrees this boosts the work per cycle by a factor of two, compared to existing techniques (see figure).

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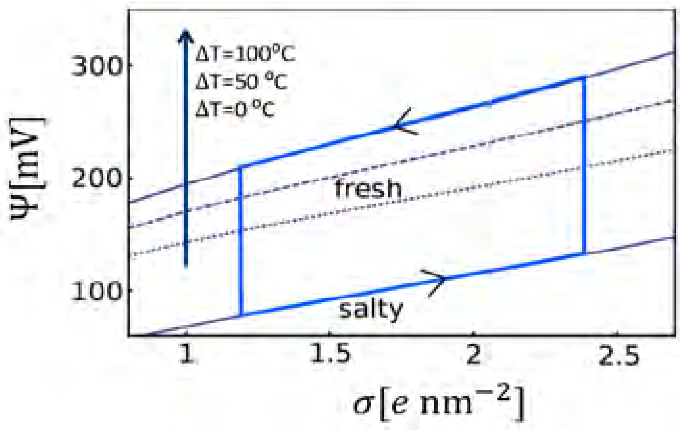

Figure: Blue energy cycle in the potential – charge representation. Stroked lines represent the upper part of the cycle, connected to fresh water reservoirs of different temperature.

Structural and size effects on the desalination cycle of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigate the effect, which varying pore and engine sizes have on the properties of the desalination cycle. To obtain comparative results, we introduce the size ratio x=Vb/(Vb+Ve) between the volume Ve of the capacitive engine and Vb of the bath, which is desalinated. By this, we compare desalination cycles, which are obtained by using electrodes, completely build of pores with a certain fixed size. We find that the size ratio x does effect the amount of energy that is needed to desalinate one liter of water; interestingly, the desalination cycle becomes optimal for very large ratios x, when the desalination bath becomes very large in comparison to the engine (see figure). Thereby, the required energy can vary by more than 15 percent.

Furthermore, the optimal pore size also depends on the size ratio x. We discuss this behavior and physical as well as economical limits of this optimization. Finally, our findings can easily be mapped onto the inverse cycle, a blue engine, which allows a maximization of the harvested blue energy.

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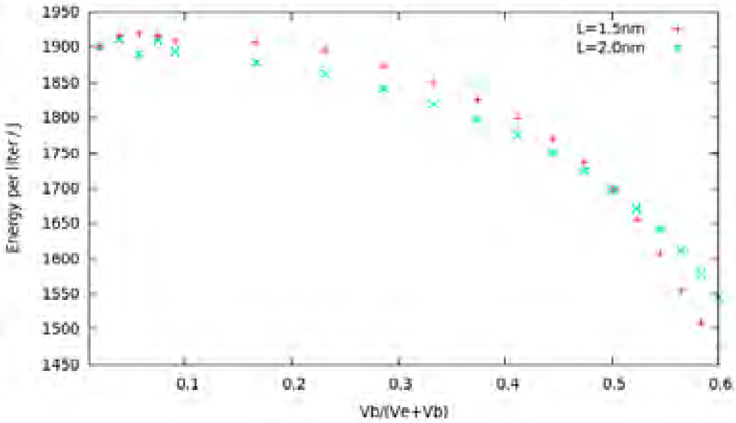

Figure: Required energy for the desalination of one liter of sea water, shown against the ratio x=Vb/(Ve+Vb) for fixed pore sizes L.

Membrane Capacitive Deionization: definitions and double layer modeling

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Membrane Capacitive Deionization (MCDI) employs ion-exchange membranes together with porous carbon electrodes to desalinate water. In MCDI ions are stored both in the interparticle pore space between carbon particles, as well as within the electrical double layers (EDL) formed inside the carbon micropores. In the micropore EDLs, electronic charge in the carbon is exactly matched by the ionic charge in the water-filled micropores (diffuse or Donnan layer), see Fig. 1. The main advantage of MCDI is that the charge efficiency is much higher than in CDI, at low enough salt concentration approaching unity. This leads to a reduction in energy consumption. Also, in MCDI a reversal of the voltage is possible during discharge (regeneration), which helps to speed up ion release. In CDI, voltage reversal lead to a frequency doubling of the CDI cycles. Finally, in MCDI it works better than in CDI to operate in constant-current mode, leading to a stable effluent salt concentration at a level that can be tuned by modifying the current.

In the presentation we discuss different meanings of terminology used in the CDI-field for efficiency: charge efficiency, current efficiency, Coulombic efficiency, and salt removal efficiency. We compare electrostatic double layer models that can be used to describe ion adsorption and charge (Gouy-Chapman-Stern versus modified-Donnan model). Finally, we describe how these microscopic EDL-models can be included in a two-dimensional electrode transport model.

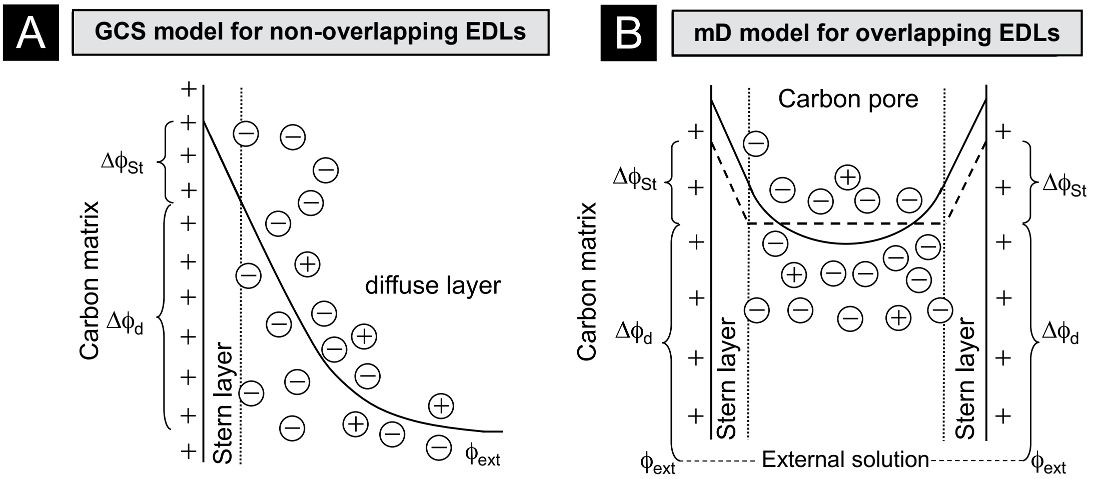

Fig. 1. Classical Gouy-Chapman-Stern EDL model vs modified-Donnan model for carbon micropores.

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Multiphysics simulation of Membrane Capacitive Deionization for mixed streams

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Membrane capacitive deionization (MCDI) has emerged over the past years as an energy- and cost-efficient technology for desalination of waters with low to moderate salt content in applications such as domestic water softening or desalination of cooling tower make-up water [1]. With the aim of broadening the range of applications of this technology, we have been investigating the possibility of MCDI treatment for more 'complex' wastewaters and industrial process streams - such as biomass hydrolysates [2] - which contain both salts and organic compounds. This combination tends to be problematic for conventional separation processes; therefore there is a need for new techniques for efficient recovery of the target compounds and/or water. The low fouling susceptibility and high energy efficiency of MCDI make it a potential alternative separation technology for such types of streams. Initial tests indicated that the current commercial MCDI setups do not always operate optimally in the presence of organic compounds. Therefore a better understanding of the behavior of different types of organics within MCDI, and of the key factors determining overall performance on mixed streams is needed, in order to develop tailored designs and operational modes.

In the coming future, the goal of this research is to develop a COMSOL multiphysics FEM model to develop insight into the transport processes occurring in MCDI applied to mixed streams, and subsequently use this model as a design aid for novel applications.

Points of attention are CFD-based geometry optimizations to minimize dispersion (in order to e.g. enhance product recovery), strategies for mitigating concentration polarization effects on both the spacer and electrode side of the membrane, prevention of faradaic reactions, fouling, scaling and clogging, and selection of ion exchange membranes with an optimal balance between mobility of organics and electrical resistance.

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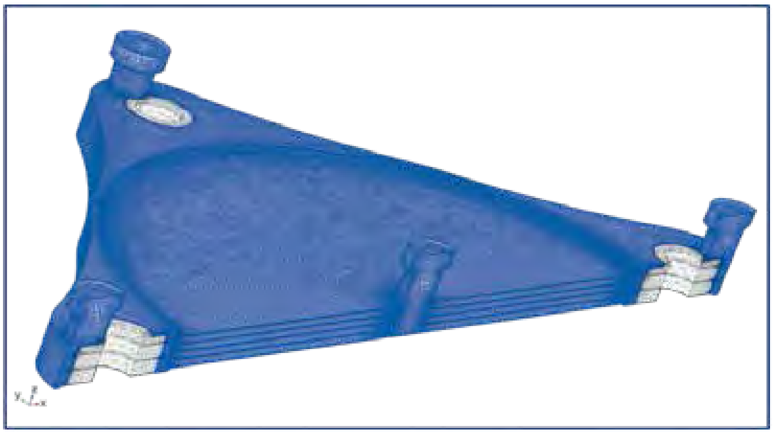

FEM geometry of an experimental CDI cell

Is solution chemistry responsible for clay particle mobility through soil pores?

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Clay particles mobility in soil is responsible for preferential transfer of various contaminants and for the soil textural differentiation at the pedological time scale. The aggregation and dispersion mechanisms of clay particles are expected to play a major role in this transfer. However, these mechanisms have mostly been studied for pure and well-crystallized “model” clay minerals, and through wide physico-chemical conditions, poorly representative for those encountered in soils.

In this work, we studied the respective impacts of pH and salt concentration on the colloidal behavior of pedogenetic smectite particles originating from a Luvisol. Both static and dynamic approaches were used considering (i) a time lapse of 1 to 5 hours that corresponds to the duration of a physico-chemical perturbation caused by infiltration of gravitational water along a rain event; (ii) a pH range of 4 to 8; and (iii) $CaCl_2$ concentration range from 10^{-5} to 10^{-3} M, in order to be representative for the conditions encountered in the soil solution. Aggregation and dispersion kinetics were measured by time resolved laser diffraction, complemented with electrophoretic mobility analyses. The structural organization of clay particles and aggregates was studied using X-ray diffraction, cryogenic SEM and static light scattering. Finally, percolation experiments through saturated diffusion columns were attempted to estimate the role of these physicochemical interfacial reactions on the behavior of clay particles at the scale of the porous medium. Based on these experiments, we drawn a phase diagram for soil clays as a function of pH and calcium concentration, and identified the mechanisms and kinetics associated to the formation of the respective states. We showed that soil particles behavior in suspension is similar to that recorded for model clays; and that the aggregation and dispersion mechanisms related to pH and/or calcium modification are enough rapid to occur through the time scale of gravitational water (with the exception of dispersion induced by salt dilution), and thus within soil porosity. Considering the overall soil system, these physico-chemical processes have to be balanced with additional driving effects such as rainfall intensity and frequency and inhomogeneous pore structure, both leading to varying active porosity.

Acknowledgment

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Sorption of tylosin on goethite

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Tylosin (TYL), a widely used veterinary antibiotic, was often employed ad feed additives in poultry and swine farms. During the application of livestock wastes on agricultural fields, TYL might be persistent in soils or transport to groundwater and contribute to the growth or development of antibiotic-resistant microbial populations [1], it was necessary to understand the fates of such antibiotics in environmental systems. Prior studies revealed that the fate and transport of antibiotics in the environment would be affected by the interactions between chemicals and soil minerals [2]. In order to understand the contribution of goethite on the environmental fate of TYL and assess the sorption behavior and mechanism of TYL on goethite accurately, we investigated the influences of solution chemical factors (pH and ionic strength) on the sorption of TYL on goethite through a series of batch experiments. The sorption data were fitted by Freundlich model and dual mode sorption model. It was obvious that sorption was strongly dependent on pH and ionic strength. Sorption capacity of TYL increased as the pH increased and ionic strength decreased. The pH and ionic strength-dependences might be related with the specific complexation between cationic/neutral TYL and goethite. Spectroscopic evidence indicated that tricarbonylamide and hydroxyl functional groups of TYL might be accounted for the sorption on mineral surface. The experimental data of TYL sorption could be fitted by surface complexation model (FITEQL), indicating that ≡FeOH with TYL interaction could be reasonably represented as a complex formation of a monoacid with discrete sites on goethite. It should be noticed that the heterogeneous of sorption affinity of TYL on goethite at various environment to assess its environment risk.

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Acknowledgment

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Effect of pyrite interface on silver and mercury behavior in natural porous media

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Interactions of heavy metals at liquid-solid interfaces have been largely studying by the scientific community due to their crucial role for understanding environmental pollution owing to the various human activities: metallurgy, dentistry, chemistry, nuclear industry, paint and batteries, and agricultural habits. To prevent migration of heavy metal pollutants in wastewater, contaminated soil and solid wastes, knowledge of mechanisms controlling transport and transfer of metals which occurs at the solid-liquid interface is thus a prerequisite. Possible mechanisms are numerous: precipitation, dissolution, sorption, complexation, redox, etc. In subsurface environment, sulfide compounds such as pyrite are very often present. Due to their high surface reactivity and their redox properties they can thus control the fate of trace elements even when this mineral is present at low concentration. For better understanding its role, batch and column experiments were performed in the presence of silver or mercury with natural porous media, quartz sand and schist, which both contained some pyrite. From experimental results with natural materials, we observed a strong pH-control by pyrite in the first part of experiments due to its redox dissolution with high release of Fe. After some delay, the presence of calcite buffers the pH due its dissolution too. At the same time, we showed that sorption of Ag(I) is kinetically limited. At equilibrium, Ag(I) sorption behavior depends strongly on pH with isotherm shapes characteristic of Langmuir-type relationship. From speciation calculations, Ag(I) sorbs mainly on iron (hydr)oxides and silanol surface sites. On the other hand, strong complexes between Ag(I) and thiosulfates are formed due to oxidative dissolution of pyrite contributing to decreasing Ag sorption capability. SEM-EDS analyses highlighted the surface complexation-precipitation of Ag_2S and Ag(0) colloids which confirmed the important role of pyrite on Ag(I) speciation. On the contrary, mercury which is sorbed at the pyrite interface blocks the surface site oxidation: no change in the oxidation state of Hg(II) was observed. From all the experiments and XPS surface analyses, we showed that depending on the type of metal which is present, surface reactivity of pyrite can change by increasing either adsorption or redox precipitation of trace metals.

Keynote

Flow-through electrode capacitive desalination and experimental characterization of desalination electrodes

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Capacitive deionization (CDI) is a novel approach to water desalination which is attracting significant and growing research attention [1,2]. A CDI cell typically consists of two porous carbon electrodes between which feedwater flows through an open channel or porous dielectric separator [3]. Charging the electrode pair to a voltage difference of approximately 1 V causes salt ions in the feedwater to transport to, and be electrostatically held against, oppositely charged carbon surfaces. In this lecture, I will describe the development of what we termed “flow-through electrode capacitive desalination” [4]. In this system, the feedwater flows directly through the porous electrodes themselves rather than between the electrodes. While flow-through electrodes for desalination were first proposed in the 1970’s [5], the systems developed at that time suffered from electrode degradation and limited performance. Now, 4 decades later, we have developed a novel, high performance flow-through electrode capacitive desalination system utilizing newly developed hierarchical carbon aerogel monolith electrodes. The pore structure of this electrode material is designed to allow for simultaneously high salt sorption and efficient fluid flow-through. I will describe the physical principles and prototype results demonstrating that flowing through (rather than between) the electrodes enables significant advantages in both desalination time and feed concentration reductions.

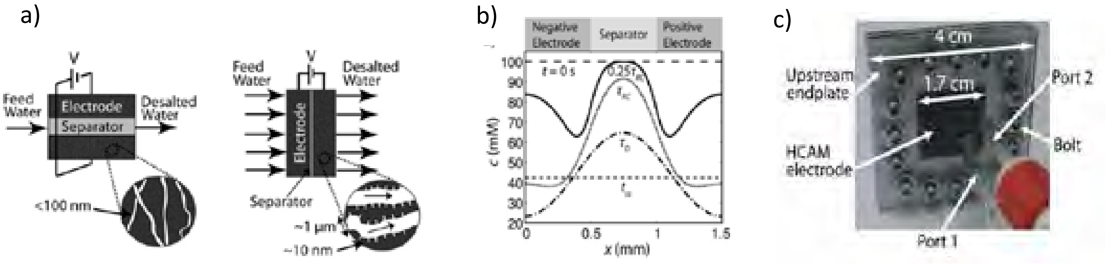

Figure 1: a) Schematic of the concept of flow through electrode capacitive desalination versus typical flow between CDI cells. b) Porous electrode transport model results demonstrating the evolution of salt concentration in a complete and charging CDI cell. c) A picture of our fabricated flow through electrode capacitive desalination prototype.

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In the second part of the lecture, I will discuss our recently developed experimental techniques to characterize and study CDI cell and porous electrode performance. Characterization of CDI systems typically involves measurements of the downstream (treated) water conductivity [1,2,3]. However, the conductivity data obtained can often be dependent on a large number of system and flow parameters, and is not well suited to detect effects such as variations in sorption performance between electrodes. We have developed several unique tools which allow for improved and more insightful studies of CDI systems, and thus can be used to catalyze future performance improvements. These include a first time measurement of spatially resolved chloride salt concentration between charging electrodes in a CDI cell (using fluorescent microscopy), and a framework for electrochemical impedance spectroscopy (EIS) studies of multiscale porous electrodes [6,7]

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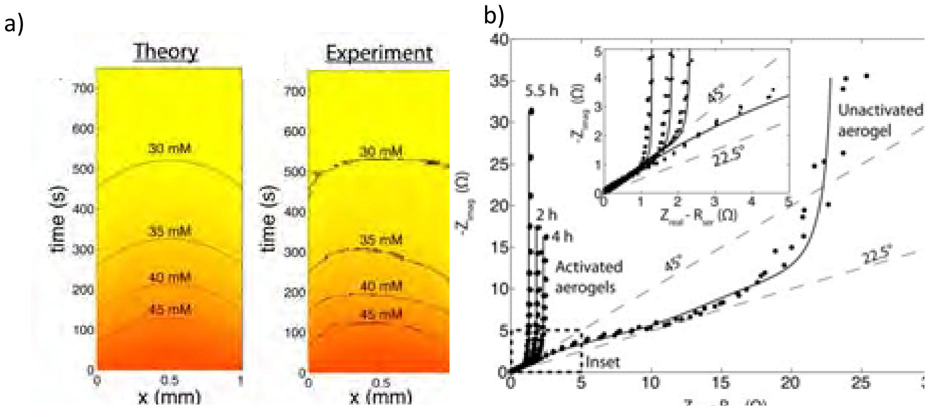

Figure 2: a) Theoretical predications and direct measurements of spatially resolved salt concentration between charging porous electrodes of a CDI cell. b) Circuit model predictions (black lines) and measurements (black dots) of the impedance of porous electrodes with multi-scale pore structures for CDI.

Enhanced energy efficiency in increased discharging voltage Capacitive Deionization

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Capacitive deionization (CDI) is an electrochemical method for water desalination employing porous carbon electrodes. In the porous carbon electrodes, electrical double layers are formed, which consist of two phases: the electron conductive matrix, in which electrons are stored, and the diffuse layer, in which ions are stored to compensate the electrical charge. During the adsorption phase, electrons are transported from the negatively polarized electrode towards the positively polarized electrode. To keep the electrodes electroneutral, for every electron transported, a counterion is adsorbed into the diffuse layer or a co-ion is desorbed from the diffuse layer, see Fig. 1. The desorption of these co-ions results in a charge efficiency, that is the ratio of salt adsorbed over the electrons transported from the positively polarized to the negatively polarized electrode, below unity. A charge efficiency below unity results in higher energy demands, because more electrons are transported per salt molecule removed from the brackish water, and is therefore disadvantageous.

We show how the charge efficiency can be increased by increasing the discharging voltage, such that we can avoid the adsorption of co-ions in the porous carbon electrodes during the desorption phase. Consequently, these ions cannot be desorbed during the adsorption phase either.

We conducted experiments employing electrodes made of commercially available microporous activated carbon. We applied a constant charging voltage of 1.2 V during the adsorption phase and different constant discharging voltages from 0 V up to 0.9 V during the desorption phase. Our experiments were conducted in flow-by mode, that is, the water flows through a spacer channel in between the two oppositely polarized electrodes. The adsorption and desorption time of all the experiments was 1200 s, so that, at the end of each adsorption and desorption phase, there was no net transport of electrons and ions to and from the electrodes. We cycled three times through the adsorption and desorption phase before actually collecting the data, so the salt adsorption and the charge density did not differ between one and the other cycle. The experiments were performed with three different inflow concentrations of NaCl: 5, 20 and 80 mM. We compared the experimental data of the salt adsorption and the charge density with theoretical calculations using the modified Donnan model [1].

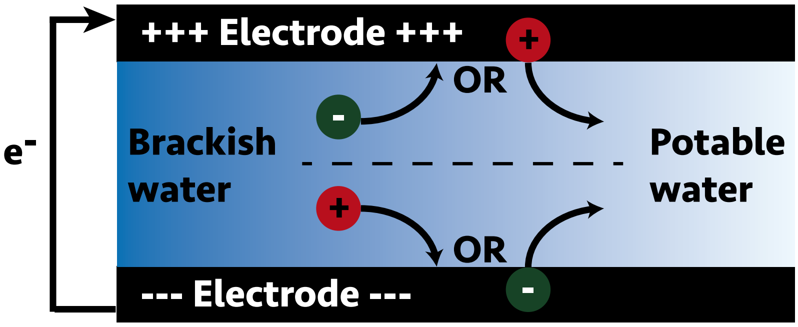

Figure 1 CDI cell during the adsorption phase. Every electron transported from the negatively polarized electrode to the positively polarized electrode results in the adsorption of a counterion into or the desorption of a co-ion from both oppositely polarized porous carbon electrodes.

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Seawater Desalination and Energy Recovery using Flow-electrode Capacitive Deionization (FCDi)

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The energy-efficient capacitive deionization (CDI) techniques have been used for desalination of low salt concentration water below brackish water and are not utilized for the seawater desalination, because it has a limited ion adsorption capacity of the fixed porous carbon electrode. To overcome the limitation of current CDI systems, we designed flow-electrode capacitive deionization (FCDi) system that uses flow-electrode. The flow-electrode, which is comprised of carbon suspension of activated carbon and 0.1 M NaCl solution, flows through a flow-path carved on the current collector instead of the fixed carbon electrode of the conventional CDI. FCDi unit cell exhibited continuous desalting performance more than 95 % of removal efficiency with respect to not only 32.1 g L^{-1} of NaCl solution but also 2.0 g L-1 of concentration. This result demonstrates that the flow-electrodes, fed in the FCDi cell, have infinite ion adsorption capacity and allow continuous seawater desalination. Also, we observed that energy supplied during charge step can be recovered by constant current discharge of flow-electrode, which is fully charged at various voltages.

Wednesday

11.10 - 12.10
BENTACERA ZAAL

Labilities of aqueous nanoparticulate metal complexes

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An inherent property of a dispersion of charged nanoparticles (NPs) is that their charges and reactive sites are spatially confined to the particle body which is at a potential different from that in the bulk medium. This feature has important consequences for the reactivity of nanoparticulate complexants: the diffusive rate of reactant supply is lower as compared to molecular complexants, whilst the local concentration of reactant ions may be enhanced if the particle's electric field has the opposite charge sign. Thus the uptake and release kinetics of small ions and molecules by NPs can differ significantly from those with molecular ligands, or larger colloidal entities.[1] These effects are most dramatic for soft NPs, for which the electrostatic accumulation mechanisms operate on a 3D level.[2] Accordingly, appropriate theory is needed to describe and predict the lability of nanoparticulate complexes, i.e. the extent to which nanoparticulate compounds may dissociate to release free target compounds which then contribute to signals measured by dynamic speciation sensors, uptake by organisms, or accumulation at reactive interphases. The notion of lability is inherently linked to the timescale of the process under consideration. A theoretical framework is presented that describes the lability of metal-NP species over a range of effective timescales. The concepts are illustrated by electrochemical stripping data on metal complexes with natural soft nanoparticles of humic acid.[3]

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Wastewater effects on soil-organic compound interactions, non-typical sorption isotherms and clay vs. SOM as sorbing phases

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Soils are well-known to act as natural barriers preventing the contamination spreading and, therefore, may accumulate pollutants. Drastic soil pollution may be induced by wastewater from olive oil production (olive oil mill wastewater, OMW). The OMW land disposal affects the soil/water environment by inducing toxicity, contaminating ground- and surface water sources, reducing soil wettability and changing multiple physic-chemical soil properties. On the other hand, due to extremely high organic matter (OM) contents of OMW, the OMW-soil interactions may provide important environmental-agricultural extreme scenarios of wastewater effects on soil properties. Examining sorption of organic compounds from water on soils affected by OMW may provide an important mechanistic information on changes in soil surfaces and interfaces and also be essential for prognosis of behavior of various organic pollutants (and agrochemicals) in the soil environment. This presentation reports the selected results of the trilateral DFG-funded study on the effects of OMW applied to a series of soils on soil sorptive efficacy towards organic compounds and examines (a) the possible sorption mechanisms and (b) the important sorptive components of soils. Among others, organic compounds included typical herbicides, simazine and diuron, representing widely used agrochemicals, and the OMW-soil interaction scenarios involved the various types of OMW application, from the lab-controlled to the short-term field- or long-term scenarios. In multiple cases, the prior OMW-soil interactions involved distinct increases in sorption distribution coefficients of organic compounds thus indicating an enhanced role of soils as barriers against environmental spreading of organic pollutants. Surprisingly, there were no distinct relations between the OMW-induced changes in distribution coefficients of organic compounds on soils and the changes in soil organic matter (SOM) content. Variable shapes of sorption isotherms were obtained for organic sorbates on soils, and, in some cases, sorption isotherms demonstrated a sigmoid shape (Figure) which suggested cooperative interactions of sorbates with the soil sorbents. However, the presence of a sigmoid shape was not related necessarily to the prior OMW-soil interactions. Observed cooperative sorption expressed by a stepwise change in an isotherm might reflect the changes in the soil matrix including both SOM and clay components. The data analysis suggested the significance of the soil's mineral clayey fraction for sorption of agrochemicals from water. In this way, the consideration of SOM as a major soil sorbent for multiple non-ionized organic compounds, and, specifically for agrochemicals - herbicides, seems to be challenged.

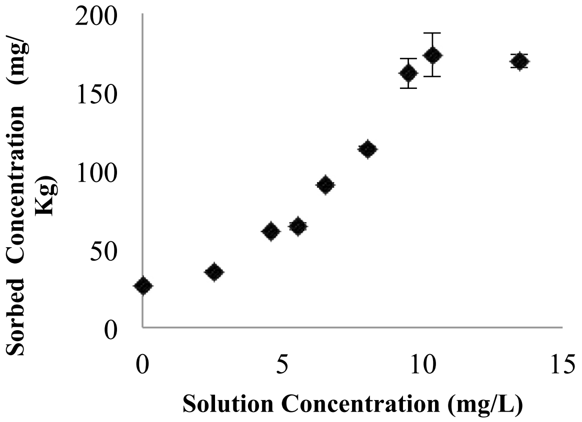

Figure. Diuron sorption isotherm on loamy sandy soil affected by OMW

Arsenic Adsorption: Effect of pH, Natural Organic Matter and Oxides Composition

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Surface complexation (adsorption) reactions strongly influence behavior of arsenic in the natural environment. For oxyanions, metal (hydr)oxides and clay edges are the most important reactive surfaces in nature. Arsenate (As(V)) binds much stronger than arsenite (As(III)) to the surfaces of metal (hydr)oxides. In addition to arsenic speciation, the adsorption is also controlled by pH, calcium and phosphate adsorption, presence of natural organic matter (NOM), and composition and reactive surface area of the surface. Due to this complexity, results obtained from single component system cannot be directly applied to predict arsenic adsorption in natural samples. In this case, advanced surface complexation models are powerful tools in understanding and predicting behaviour of pollutants such as arsenic in the environment.

The pH dependent solid-solution distribution (solubility) of arsenic in five Dutch soil samples spiked with arsenate was measured in the pH range 4–8, and the results were interpreted using the LCD (Ligand and Charge Distribution) adsorption modeling. The Ligand and Charge Distribution model (LCD) combines surface complexation models for both oxides and natural organic matter, which allows for consistent description of multi-component adsorption to oxides, and takes also into account the effect of natural organic matter that is present on oxide surface.

(1) Arsenic in soil shows a minimum soluble concentration around pH 6–8. This pH dependency can be successfully described with the LCD model and it is attributed mainly to the synergistic effects from Ca adsorption. In the presence of bivalent cations (e.g. Ca^{2+}), solubility of arsenate is the lowest around neutral pH.

(2) Presence of natural organic matter adsorbed on the surface competes strongly with arsenic and significantly increases arsenic solubility. A change in the organic matter loading will therefore lead to a change in arsenic distribution.

(3) Arsenic adsorption in soils depends on the relative contribution of aluminum and iron (hydr)oxides to the total amount of metal (hydr)oxides. With increasing contribution from aluminum (hydr)oxides, adsorption of arsenic becomes weaker, whereas adsorption of phosphate is not so much influenced by the change in oxides composition. Therefore solubility of arsenic is expected to be higher in aluminum (hydr) oxides dominated systems than in iron (hydr)oxides dominated systems.

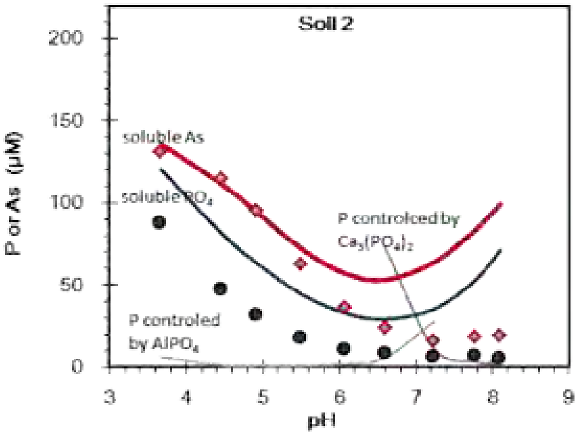

Fig. 1. Soluble arsenic and phosphate in one soil sample (Soil 2). Symbols are data and lines are model calculations.

Retention and Remobilization of Stabilized Silver Nanoparticles in Soils

Erwin Klumpp[1], **Yan Liang**[1], **Scott A. Bradford**[3], **Jiri Simunek**[4], **Marc Heggen**[2], **and Harry Vereecken**[1]
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Transport and retention of surfactant stabilized AgNP under environmentally relevant conditions was investigated by water-saturated columns packed with quartz sand and by undisturbed loamy sand soil columns with around 90% water saturation. The remobilization of retained AgNP from undisturbed soil was studied by changing the solution chemistry such as change of cation types and ionic strength reduction. Results of transport experiments in quartz sand and soil showed similar trends with regard to the effects of physicochemical factors, e.g., enhanced transport with decreasing solution IS, increasing AgNP input concentration and flow velocity. In contrast to the conventional filtration theory, retention profiles (RPs) in sand exhibited uniform, nonmonotonic, or hyperexponential shapes that were sensitive to physicochemical conditions, while significant retardation of AgNP breakthrough and hyperexponential RPs were observed in almost all the transport experiments with soil. Results from remobilization experiments indicated that further release of AgNP and clay from the soil was induced by cation exchange (K^+ for Ca^{2+}) that reduced the bridging interaction and IS reduction that expanded the electrical double layer. Transmission electron microscopy, energy-dispersive X-ray spectroscopy, and correlations between released soil colloids and AgNP indicated that some of the released AgNP were associated with the released clay fraction.

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The role of soil-borne DOC on the aggregation of synthetic Ag nanoparticles in soils

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Synthetic inorganic nanoparticles (NP) enter the soil through different pathways, where their stability is affected by various processes. Sorption to silica surfaces is reported to decrease with increasing negative particle charge (Thio et al., 2012). Several publications indicate an increased NP stability following DOC sorption (Lecoanet et al., 2004). Therefore, we tested the following hypothesis: (A) Bare AgNP show stronger sorption to soil particles than those stabilized through additional charges. (B) The colloidal stability of NP is increased through the sorption of soil-borne DOC. (A) We conducted batch experiments using silt and differently stabilized (bare and citrate-coated (i.e. additionally charge stabilized) AgNP) AgNP at pH 6.5 and initial Ag concentrations (c_0) ranging from 30 to 500 µg/L. After 24 h of end-over-end-shaking and filtration (1.2 µm) the Ag concentration (c_{Ag}) was determined in the filtrate. The concentration of sorbed Ag was determined through the difference between c_0 and c_{Ag}. Results of both NP showed sorption curves with similar slopes, suggesting that particle charge does not control sorption. (B) Bare and citrate-stabilized AgNP were suspended in a centrifuged soil solution (cut-off 10 nm). Zeta potential and sorbed amounts of DOC were determined after 24 and 48 h. The optical density of the soil solution was determined at $\lambda = 254$ and 410 nm before and after DOC sorption. Results of bare AgNP showed high DOC sorption after only 24 h along with an increase in particle charge and particle size. Short-chained DOC played a more dominant role in sorption to AgNP than longer-chained DOC. In addition, aggregation kinetics of citrate-stabilized AgNP were determined in suspensions with different AgNP concentrations following the addition of (i) extracted soil solution and (ii) Ca-solution to obtain the same final concentration as in the soil solution (1.5 mM Ca). While at 0.5 and 5 mg/L Ag, the two treatments did not differ significantly in their particle size, at a Ag concentration of 10 mg/L, AgNP exposed to soil solution showed lower particle sizes than AgNP exposed to Ca solution, suggesting that the stabilizing effect of DOC is relevant especially at high AgNP concentration. Scanning electron micrographs are being prepared to further analyse the state of aggregation as affected by organic ligands.

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Silver nanoparticle-based water treatment: mechanistic aspects and technology viability

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A number of water treatment technologies based around use of silver nanoparticles are now on the market yet uncertainty remains as to their mechanism of operation, efficacy and long-term viability. Here we summarise what is known of their mechanism of bactericidal activity, the factors determining their lifetime and, from these insights, provide advice on the overall viability of the technology. In particular, attention is given to i) the impact of both the method of formation of the silver nanoparticles and nature of the solid support on bactericidal activity with X-ray spectroscopic techniques used to determine the redox state and molecular-level structure of the materials produced and ii) analysis of the factors contributing the differences in both toxicity and longevity. In addition to insights into factors controlling oxidative dissolution kinetics and resultant production of silver ions (recognized to be a key determinant of toxicity), attention is also given to factors that may contribute to Ag-mediated reactive oxygen species production (He et al., 2011, 2013a,b).

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Ultrasound-assisted Preparation of Electrospun Carbon Nanofiber/graphene Composite electrode for Capacitive Deionization

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The capacitive deionization technology (CDI) has drawn much attention because of its potential as an energy-efficient alternative for producing fresh water from salted water sources. For the CDI technology, the electrode materials with tuned pore structure and functionality such as conductivity are the key to the efficient desalination process. In this talk, we report on the design and fabrication of electrospun carbon nanofiber/graphene (CNF/G) electrodes by electrospinning polymer nanofibers, in which graphene oxide was sprayed simultaneously, and the composites were heat-treated. The freestanding carbon nanofiber web acts as a framework for sustaining graphene, and helps to prevent the agglomeration of graphene, while the graphene helps to improve the conductivity of the as-obtained CNF/G composites that exhibit an electrosorption capacity for NaCl of 15 mg/g, which is about 2.5 times of the adsorbed amount in the case of the pristine CNF without graphene. This has demonstrated that the graphene is indispensible for making high perforamnce CDI electrodes with desired structure and capacity.

Keywords: Carbon fiber, Electrospinning, Graphene, Capacitive deionization

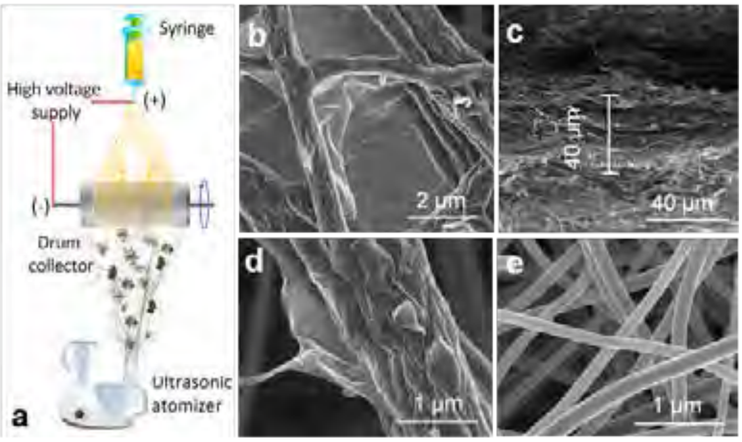

Figure 1 (a) Schematic of the electrospinning coupled with ultrasonic spray process, (b) top-view and (c) side-view SEM images of the as-prepared CNF/G, (d) SEM image of the individual CNF/G fiber at higher magnification, and (e) SEM image of the pristine CNF.

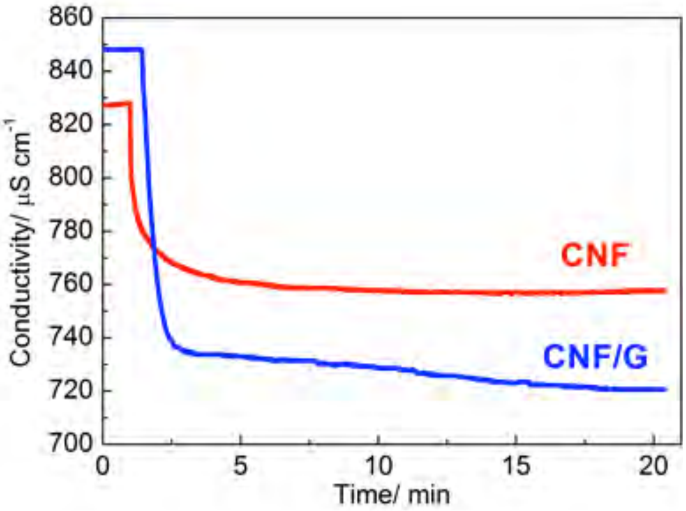

Figure 2 Desalination curves of CNF and CNF/G electrodes as a function of time in CDI, for which the test conditions are: the cell voltage, 1.2 V; the flow rate of water, 15 mL/min.

Capacitive deionization (CDI) of NaCl solution using activated carbon electrodes in a novel CDI module

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A novel CDI module is introduced using activated carbons as electrode in capacitive deionization process. Voltage is not applied to each electrode as in the common CDI module but rather on the metal plate outside the entire module. The **effects of voltage and electrode pair number on the performance of the novel CDI module are** investigated, and the **novel CDI module is compared with the common CDI module.** The experimental results show the novel CDI module exhibits higher electrosorption capacity, shorter desorption time, and lower energy consumption than those of common CDI module.

Keyword: Capacitive deionization, electrosorption, module

Keynote
Salt removal, water recovery and energy consumption in Membrane Capacitive Deionization

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Membrane Capacitive Deionization (MCDI) is an emerging new electrochemical desalination technology, which is suitable for the removal of ions from brackish water up to concentrations of about 100 mM (ca. 5000 ppm). In MCDI ions are removed from feed water by applying an electrical potential difference between two electrodes, whereby an ion-exchange membrane is positioned in front of each electrode. Water can flow in the spacer compartment, which is situated between the oppositely charged electrodes. Ions that are removed from the feed water are temporarily stored in the electrical double layers that are formed at the electrode-water interface. In MCDI, the co-ions that are expelled from the electrical double layers cannot enter the flow channel because they are blocked by the anion and cation exchange membranes. These co-ions are therefore retained in the interparticle space in the electrode compartment. Because of charge neutrality these co-ions need to be compensation for by counterions, which pass the ion exchange membrane from the spacer compartment. In MCDI, the expelled co-ions therefore lead to an increase of the total ion storage capacity of the electrodes.

The electrodes need to be regenerated once they are saturated with ions, which can be done by reducing or even reversing the applied voltage. In MCDI, the released counterions cannot migrate to the opposite electrode, because of the presence of the ion exchange membranes. Therefore, during electrode regeneration high concentrations of salt ions can be obtained in the flow compartment, which can subsequently be flushed out with a small amount of water, resulting in high water recoveries.

Dividing a feed-water stream into a dilute stream and a stream concentrated in ions costs energy and for any desalination technology the energy consumption is a significant part of the Total Cost of Ownership. In MCDI, the electronic charge is fully charge balanced by counterion adsorption and the charge efficiency, which is the ratio of the ionic charge over the electrical charge, is therefore (close to) unity. As a consequence the energy use is directly proportional to the amount of ions that are being removed from the feed water.

In this paper we discuss experimental results of a MCDI operation which shows how MCDI is ideally suited to achieve both high ion removal efficiency and high water recovery, which makes this an attractive technology for many applications. Furthermore, we also present data for the energy consumption at different salt concentrations and salt removal levels. We demonstrate that up to 83% of the energy used for charging the electrodes during desalination can be recovered in the electrode regeneration step. This can be achieved by charging and discharging the electrodes in a controlled manner by using constant current conditions. By implementing energy recovery as an integral part of the MCDI operation, the overall energy consumption can be as low as 0.26 (kW·h)/m^3 of produced water to reduce the salinity by 10 mM. In comparison, by using reverse osmosis under similar conditions the energy consumption is about 1kWh per m^3 of produced freshwater. This means that MCDI is more energy efficient for treatment of brackish water than reverse osmosis.

POSTER PRESENTATIONS MONDAY

Treatment of the Pharmaceutical effluent by Membrane Bioreactor

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The issue concerning the presence and potential risks micro pollutants in the environment has become a topical issue. Today, the wastewater treatment plants are not able to adequately treat this new type of pollution. Eliminating pharmaceutical residues is possible with advanced technology using chemical and physical processes such as membrane filtration, adsorption on activated carbon or advanced oxidation processes. Currently, several studies are conducted to study and optimize the disposal of pharmaceuticals by membrane bioreactor. The objective of this study is to evaluate the potential for the membrane bioreactor degradation pharmaceutical effluents containing high load of pollutants collected from different sources. Proposed in the case of discharges from the manufacturing workshop ointment (mycoside molecule) in the case of the pharmaceutical plant. It was found that the pharmaceutical is loaded effluent carbonaceous pollution, nitrogen and phosphate. For the removal of these pollutants we opted for a coupling of physico-chemical processes (coagulation flocculation), adsorption on activated carbon and membrane bioreactor. The results showed the removal rate 96.86% of COD, 69.12% in turbidity, 59.48% in nitrate, 28.84% in nitrite and 58.70% in phosphate.

Effect of granular size and activation level of activated carbon on adsorption and desorption of micropolutants

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Introduction. Pharmaceuticals and other micro-pollutants are not sufficiently removed during conventional wastewater treatment (Verlicchi et al., 2012). Activated carbon (AC) addition could form a solution (Boehler et al., 2012), although the AC would need to be periodically replaced due to saturation. In Biological Activated Carbon (BAC) the AC is continuously regenerated though desorption and biodegradation. This study investigates which type of carbon is most suited for BAC systems. The carbon should have a high adsorption capacity and allow for desorption at the threshold concentration achieved by the microorganisms.

Materials and methods. Adsorption and desorption isotherms of pharmaceutical metoprolol (MET) on 9 types of special resin-derived AC were obtained. The AC varied in granular size and activation level (Table 1).

Table1 Matrix of AC used for adsorption/desorption experiments (AC dose 0.4 g/l)

	Granular size, µm	**Activation level**	**Surface area, m2/g**		**Granular size, µm**	**Activation level**	**Surface area, m2/g**
Carbon 2 (C2)	250-355	40C	1200	**Carbon 7 (C7)**	1000-1400	20C	900
Carbon 3 (C3)	250-355	63C	1500	**Carbon 8 (C8)**	1000-1400	38C	1200
Carbon 4 (C4)	500-600	24C	900	**Carbon 9 (C9)**	1000-1400	58C	1500
Carbon 5 (C5)	500-600	40C	1200				
Carbon 6 (C6)	500-600	63C	1500				

Results and discussion. The isotherms corresponded to the Freundlich model: constants K_f and n are presented in Figure 1. The increased granular size of activated carbon resulted in decreased adsorption capacity. The transport through macro/mesopores to micropores was prolonged due to increased diameter of activated carbon beads. The adsorption capacity was positively related to the activation level – due to the larger surface area, developed during activation process in carbon dioxide environment.

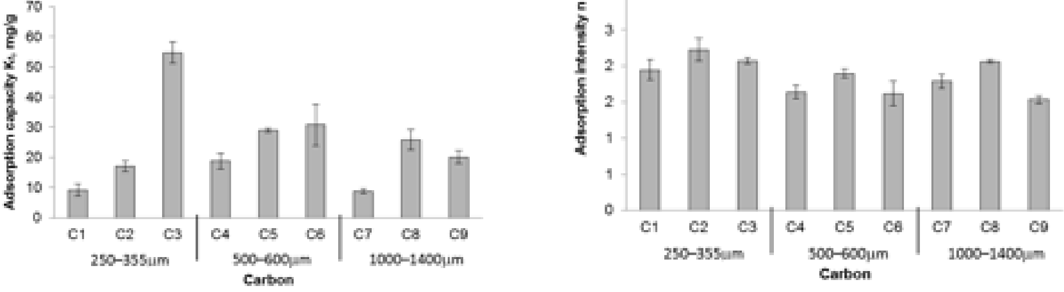

Figure 1 Effect of granular size and activation level of AC for adsorption capacity (K_f) and intensity (n)

There was no clear correlation between granular size, activation level and adsorption intensity. For a given level of carbon saturation, the equilibrium concentration for desorption was circa 10 times lower than for adsorption. Therefore these carbon types have a poor desorbability and are not suited for BAC applications.

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Aerobic Granulation in a Hybrid Reactor

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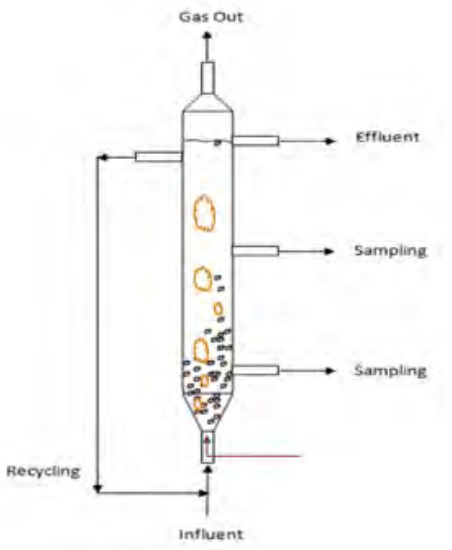
Anaerobic granulation has been studied for decades beginning with the use of Up-flow Anaerobic Sludge Blanket (UASB) reactor for anaerobic treatment of wastewater. However the application of this technology is greatly limited by drawbacks such as the inability to use it for nutrient removal and for treatment of low strength wastewater. To overcome these weaknesses, recent research efforts have been dedicated to developing aerobic granulation technology. Almost all recent studies on aerobic granulation have been on sequencing batch reactors (SBRs).

The hybrid reactor (HAR), which uses self-immobilized microbial granules under fluidized conditions, was developed at the Department of Biochemical Engineering and Biotechnology, IIT Delhi for biological treatment of wastewater. It combines the advantages of a UASB reactor and AFBR and has been successfully used for the anaerobic treatment of wastewater and biological denitrification of wastewater. Unlike the SBR, which includes batch fill-draw cycles, continuous operation is possible in an HAR. Moreover the operational sophistication in the HAR are closer to conventional treatment processes. Further the large gas–liquid interface in the HAR reduces the required volume of air for aeration. Higher level of maintenance associated with more sophisticated controls, automated switches, and automated valves as in a SBR is also not required.

To study the aerobic granulation in the HAR for simultaneous nitrification and denitrification, the reactor was aerated at the rate of 0.2-0.3 vvm. Synthetic wastewater was used for the study.



It was possible to achieve structurally stable granules within 45 days of reactor start-up. The diameter of the granules varied up to 4.5 mm with a mean diameter of around 3 mm. Our previous studies on microbial granulation for denitrification showed that the microbial flocs granulated within 15 days of reactor start-up and had a mean diameter of 1.4 mm. The larger diameter granules in the aerobic reactor may have been due to the spatial arrangement of the nitrifiers in the outer sphere and denitrifiers in the inner core in the aerobic reactor. The delay in the granulation may have been due to the higher shear associated with aeration. Of the three reactors studied, granulation was observed in reactor R1 and R2. However, the granules formed in the reactor R2 were more prone to coagulation due to the low shear at the periphery of the reactor. Results show the possibility of aerobic granulation in the hybrid reactor.

Table showing the effect of reactor geometry on granulation. A is the diameter of the cylinder. B is the diameter of the inlet tube. C and θ are height and angle of the frustum cone.

Reactor	A (cm)	B (cm)	C (cm)	A/B Ratio	θ	Granulation
R1	4	1	3.5	4	23	+
R2	4	1	2.5	4	31	+
R3	4	1	1.5	4	45	-

Soils as interfaces against pollution by PPCPs: the effect of sewage sludge disposal

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Land application of treated sewage sludge is considered as an environmentally-meaningful solution of a sludge disposal and may also positively contribute to the soil quality. However, the land application of sewage sludge may become an additional pollution source in a soil-water interface due to the prior accumulation of pollutants in sludge in the wastewater treatment process. One important group of organic pollutants termed Pharmaceuticals and Personal Care Products (PPCPs) may be accumulated in sewage sludge, due to their low removal extent in wastewater facilities and hydrophobic properties, and therefore reach the field, plants and water sources. When looking at variety of PPCPs compounds, hydrophobicity and the acidic properties are often-found characteristics of the PPCP molecules that may strongly affect their interactions with soils and control the further environmental fate. The study presented is focused on two representatives of the PPCP family, triclosan and gemfibrozil, that are notable by their significant concentrations in sewage sludge and also demonstrate a series of important biological effects, e.g, antibacterial triclosan is suspected to promote the development of antibiotics-resistant bacteria. Both organic compounds behave as hydrophobic acids, and, therefore, their sorption behavior in soil environments is also of general mechanistic interest. Therefore, in this work sorption kinetics and equilibria were studied for both PPCPs on various soils incubated in the lab conditions with a series of sewage-sludge originated amendments, in order to examine the capability of soil sorbents to provide an interface preventing the further spreading of organic pollutants. The experimental data demonstrated that, following the soil – sewage sludge incubation, the sorption of both organic compounds by soil sorbents from water was strongly increased, together with the soil organic carbon (SOC) content. This suggested that despite a significant (triclosan) or almost full (gemfibrozil) ionization in solutions, soil organic matter (SOM) is the factor that controls the interactions of a given PPCP acid in a series of soils studied at their typical pHs. The simple consideration of SOM-triclosan (and -gemfibrozil) sorption interactions may be sufficient for evaluating the environmental fate of the PPCPs studied. However, in comparing between organic sorbates, the extent of ionization in aqueous solutions becomes a dominating factor in controlling sorption of hydrophobic acids by soil sorbents. Importantly, for a given organic sorbate, there was no a single relation between the sorptivity and the SOC content of the sorbents thus demonstrating (1) an impact of the SOM nature on PPCP-soil interactions and (2) specifically, an enhanced sorptive potential of organic matter in sandy soil sorbents as compared with other soils. The difference in sorptivity between soils might be related to a less rigid SOM in sandy soils as compared with clay-containing soil sorbents. Interestingly, sorption experiments on variously incubated sandy soils at different pHs suggested that interactions of molecular and anionic forms of triclosan with sandy soil sorbents may be comparable. Therefore, as distinct from a common wisdom, the sorption of organic anions by SOM sorbents may need to be taken into account.

Interaction of metribuzin with zinc organometallic compounds

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Particular chemicals like pesticides which use, in agriculture, became inescapable are engendering an environmental pollution and more particularly that of soils.

It is urgent, for preservation of public health, to reduce at most our exposure to these substances and to operate everything to reduce and control these pollutants. Some conventional adsorbing product such carbon F400 are frequently used.

The adsorption on the synthetized metal organic complexes may be a alternate technique to disinfect soils and waters polluted by pesticides and other chemicals.

In this context, some coordination compouds of Zinc were tested in the adsorption of mitrobuzin present in contaminated water. The retained organic molecules are natural products (flavonoids and purines)

The preliminary results seems encouraging and we report them here.

Preliminary study of potential use of Central Java clay, Indonesia for waste disposal liner

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The clay deposit in Central Java, Indonesia, is considered as a source for waste disposal liner do to their low coefficient permeability and widespread distribution in Central Java. This preliminary study investigated the geological, geotechnical and mineralogical properties of the founding clay in Boyolali, Central-Java region. The particle size distribution, specific gravity of the solids, and Atterberg limits, specifically the liquid limit (LL), plastic limit (PL) and plasticity index (PI) were determined according to ASTM standard practice. Mineralogical studies performed included the determination of the cation exchange capacity (CEC) and mineralogical content of samples through the X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis. The result of this preliminary investigation show that our clay may be regarded as a suitable material for waste disposal liner.

Keywords: clay, liner, permeability, mineralogy, waste disposal

Differences in the amino acid adsorption on relaxed and unrelaxed magnetite-(111) and hematite-(001) surfaces

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Magnetite (Fe_3O_4) crystallizes in the inverse spinel structure [1]. In nature magnetite is also an important biomineral. Magnetotactic bacteria, e.g., use magnetite single-crystals to orientate themselves in the earth magnetic field. The connection between the inorganic magnetite and the organic parts of the microorganism is the magnetosome membrane (MM). This membrane is built by membrane proteins which are dominated by the amino acids aspartic acid (asp), glutamic acid (glu), glycine (gly) and leucine (leu) [2,3]. Bürger et. al [4] showed that it is energetically favorable for the amino acids to adsorb on the relaxed magnetite-(111)-surface. For the current study, the relaxed and unrelaxed hematite-(001) and the relaxed and unrelaxed magnetite-(111) surfaces have been used. They are the most common surfaces of the respective minerals. Their crystal structures contain iron as Fe^{3+} (hematite) and a mixture of Fe^{2+} and Fe^{3+} (magnetite). However, in all systems studied the surface oxygen termination is the dense packed oxygen layer.

Force field simulations of the interaction distances between the iron oxide surfaces and the amino acid offer the possibility to investigate if and how the amino acids interact with the surfaces. Additionally, it is possible to investigate the interactions and the adsorption distances between the surface atoms and the functional groups of the amino acids. We have chosen the COMPASS force field because all parameters of the surfaces and of the amino acids are defined. As simulation software we used Forcite which is integrated in the Materials Studio 5.0 software package. The amino acids may adsorb in a docking box of 40.3 Å x 40.3 Å x 20 Å on the relaxed hematite-(001) surface, a docking box of 50.4 Å x 50.4 Å x 20 Å on the unrelaxed hematite-(001) surface, a docking box of 47.5 Å x 47.8 Å x 20 Å on the relaxed magnetite-(111) surface and in a docking box of 47.5 Å x 47.5 Å x 20 Å on the unrelaxed magnetite-(111) surface. The surface thicknesses are 12.5 Å, 13.2 Å, 7.4 Å and 7.3 Å, respectively. For every amino acid-iron oxide system 10,000 frames has been calculated, resulting in 120,000 frames altogether. The lowest energy systems for each combination have been evaluated.

The comparison of results of the simulations shows the differences in the adsorptions behavior. The adsorption mode switches between monodentate, bidentate and bridging, depending obviously from the amount of the iron cations and their oxidation state. The Fe-O adsorption distances between the surface Fe-atoms and the amino acids O-atoms vary between the different adsorption systems, but in all different cases the electrostatic interaction dominates the process. The conformations of all of the four amino acids vary for the different iron oxide surfaces.

In our study we show that the behavior of the iron oxides surfaces take distinct influence on the adsorption distance, the binding mode and especially the conformation of the amino acids.

Keywords: adsorption, iron oxides, force field simulation, amino acid

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Electrochemical treatment for the surface industry wastewater

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This study had like main aim the combination in the same cell of electrolysis two types distinct of treatment: the electroflotation (EF) and the electrochlorination (ECH), with an objective to eliminate the inorganic pollutants. At the time of this study, it was shown that with a wise choice of operating conditions, the cell of EF presents an excellent performance for the elimination of heavy metals. The results obtained showed that the EF is a method of separation effective for the copper reduction. Thus, it is possible to carry out rates of recoveries going up to 88.90 %, without chemical addition of additive. The examination of the effect of the operational parameters shows that the initial pH is a determining factor in the EF process. Indeed, it proves that a sufficiently high pH generates the formation of the flocs of good buoyancy what contributes to the improvement of the effectiveness of the technique. Moreover, the rise in the intensity of current makes it possible to decrease the processing time. For the treatment of the solutions Cu-EDTA by EFF, one notes the remarkable effect of the presence of the EDTA. After the elimination of the copper not complexes by EF of its precipitate, a quantity of complexes copper can be recovered with the cathode by deposit according to the content of EDTA in the solution. Oxidation by ECH showed its effectiveness for the elimination of the EDTA. Indeed, a total destruction of this pollutant can be obtained in the cell of EFF. The study also showed that the electro-oxidation of the EDTA is ensured by active chlorine produces *in sit*u. In addition to the examination of the influence of the various factors made it possible to retain that the intensity of current and the content chloride are two big factors in elimination by ECH. In addition, the tests carried out on the mixed solutions Cu-EDTA*,* indicate that coupling EF-ECH makes it possible to eliminate the organic and inorganic pollutants simultaneously. Thus, this process can constitute an alternative or a complement of the traditional methods. Moreover, this coupling presents a particular interest, because it seems to be perfectly adapted to the industry of the surface treatments, by reducing the capacity complexion of the organic pollutants, which constitute a serious constraint for the treatment of this kind of effluent, and by thus allowing the elimination of heavy metals. This not-conventional approach to the treatment of the aqueous solutions containing of heavy metals gave promising results.

Keywords: Electrochemical treatment – wastewater – Copper – EDTA

Adsorption studies of 4(tert-butyl)-1propylpyridinium bromide, ibuprofen and 4(tert-butyl)-1(carboxyethyl)pyridinium bromide onto a microporous activated carbon fabric

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Ionic liquids (ILs) possess an array of properties which are extremely low vapour pressure, high thermal and chemical stabilities and non-flammability that make them attractive for academy and industry. Initially, ionic liquids were considered environmentally friendly, but later, it has been stated that they show a wide range of environmental toxicities. Despite a lot of advantages due to their physical and chemical properties and potential applications as green solvents or electrolytes etc.., ILs are considered as emergent pollutants because their synthesis and their use at a large scale may lead to their contact with aqueous media. For the removal of ILs from water and water streams, adsorption on activated carbons is an important technology which is widely used now-a-days. In this work, we have compared the adsorption properties of ibuprofen (IBP): a pharmaceutical molecule, and two pyridinium ILs in order to better understand their adsorption mechanism on an activated carbon fabric. The ILs were chosen and designed in order to obtain organic cations with molecular size and chemical functionalities quite similar to the ones of ibuprofen.

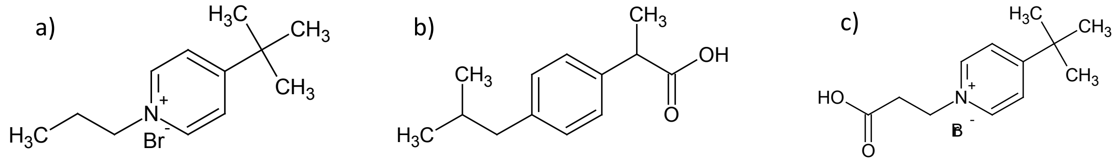

Figure 1 Developed formulas of IL1 (a), Ibuprofen (b) and IL2 (c).

Two ILs : 4(tert-butyl)-1propylpyridinium bromide (referred to IL1) and 4(tert-butyl)-1(carboxyethyl)pyridinium bromide (referred to IL2) were synthesised in our laboratory by the reaction of 4-tert-butylpyridine with either 1-bromopropane or 3-bromopropionic acid to obtain IL1 and IL2, respectively. The reactions were conducted under magnetic stirring, at room temperature for 24 hours. Products were then purified by successive washing in ethyl acetate. The final ILs product were vacuum dried for 2 days under 10^{-3} mbar in order to remove the traces of solvent and stored prior to their use under dried atmosphere. The activated carbon fabric (900-20 from Kuraray, Japan) was characterized by N_2 adsorption-desorption at 77 K and CO_2 adsorption at 273 K, pH_{PZC} (point of zero charge) measurements and acido-basic titrations (Boehm method).

The adsorption kinetics (C_0= 0.4 mmol L^{-1}) and isotherms of the single pollutants were studied at pH 3 (obtained by addition of HCl) and 7.5 (pH maintained by a 0.04 M Na_2HPO_4/KH_2PO_4 buffer) in UHQ (Ultra High Quality) water (18.2 MΩ). All the batch kinetics and isotherms were investigated by shaking (250 rpm) at a given temperature (generally 25°C) stoppered flasks (30 mL solution) containing the fabric samples (10 mg). The adsorption kinetics of an equimolar mixture of the three adsorbates (each adsorbate at C_0= 0.4 mmol L^{-1}) was studied at pH=7.5. The isotherms of equimolar binary systems IL1/IL2, IL1/ IBP, and IL1/IBP were determined by the same protocol except the use of 25 mL solutions. The organic molecules in the filtrated solutions were analyzed by UV spectrometry and HPLC. The adsorption isotherms of the molecules were studied at 13, 25 and 40°C; and the thermodynamic parameters (isoteric enthalpies, entropies and Gibbs free energies) were determined. The pore size distributions of the carbons loaded with the pollutants were determined by DFT simulations from gas adsorption isotherms, to investigate the porosity accessible to each adsorbate.

The effect of pH influences strongly the adsorption uptake. The increase in pH from 3 to 7.5 affects the charge of IL2 as its organic cation (pKa=4.1) transforms in zwitterion (carboxylate group) but the charge of IL1 remains positive. As increasing the pH from 3 to 7.5 the charge of the carbon fabric tends to decrease (pH_{PZC}=8.5), inducing a decrease in the electrostatic repulsion between the organic cations and the adsorbent that results in an enhanced uptake. The competitive adsorption in ternary mixture and binary systems were tentatively explained in term of interaction with adsorbent, and simulated in order to determine the thermodynamic parameters and to compare their values with the ones for the single adsorbate adsorption.

Orthokinetic flocculation of PSL particles with polyelectrolytes at the iso-electric point

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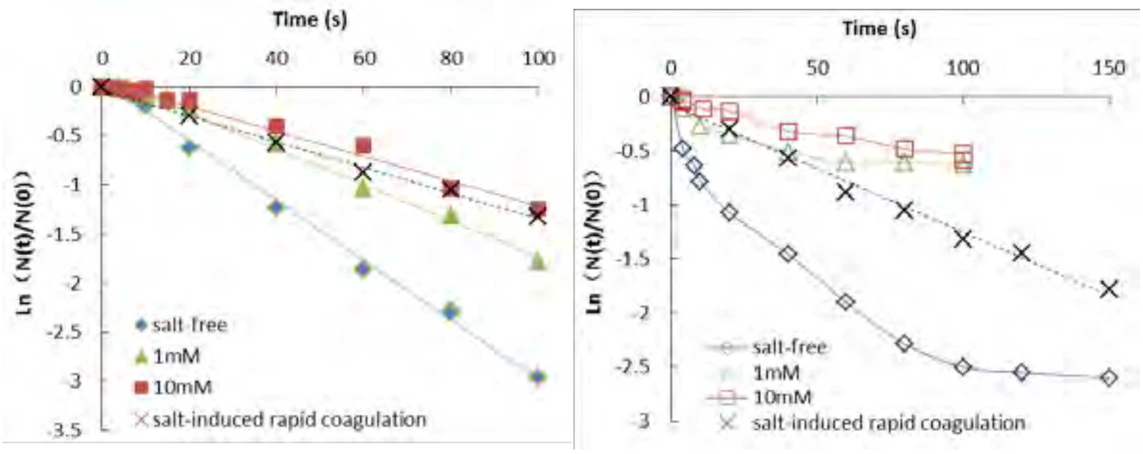
Aggregation rates of polystyrene latex particles (1956nm) induced by two positively charged polyelectrolytes, similar in the molecular weight (Mw= 5×10^6 g/mol) but different in the charge density (σ=1 and 0.04), were measured by Coulter Counter at the isoelectric point as a function of the ionic strength.

In the case of the flocculation with the high charge density polymer, an accelerated rate of flocculation was found at the isoelectric point for salt-free, 2.3 times faster than that of salt-induced rapid coagulation (observed with KCl 1M). The accelerated rate might be originated from the electrostatic attraction between bare parts of one particle and polyelectrolytes covered parts of neighboring particles, i.e. patch. Due to the screening electrostatic interaction with the increase of ionic strength the rate of flocculation decreases with increasing ionic strength and becomes the same as that of salt-induced rapid coagulation at the ionic strength of KCl 10mM.

In the case of the flocculation with the low charge density polyelectrolyte, an initial accelerated rate of flocculation followed by a subsequent stabilization was observed for salt-free. The initial acceleration can be explained by the formation of “bridges” between particles, and the stabilization should be ascribed to the steric repulsions of adsorbed polyelectrolyte segments due to further adsorption/relaxation of polymer chains on the surface. With increasing ionic strength, the rate of flocculation decreases and even becomes slower than that of salt-induced rapid coagulation. This trend indicates that the steric effect is more profound at high ionic strength.



a) b)

Figure 1 Temporal variation of the total number concentration of particles in the presence of polyelectrolytes (a) with high charge density and (b) the low charge density.

Elemental characterization of the fine colloidal and nanoparticulate fraction in stream water from a forest catchment

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Natural fine colloids and nanoparticles have the potential to encapsulate and bind nutrients. Their size range and composition is therefore relevant to understand the transport of essential nutrients like phosphorus in an aquatic ecosystem. The aim of the study was to characterize fine colloidal and nanoparticulate bound phosphorus of distinct hydromorphological areas in stream water samples from a forested experimental test site in a small headwater catchment. Asymmetric Flow Field Flow Fractionation (AF4) coupled online to inductively coupled plasma mass-spectrometry (ICP-MS) was applied for size resolved detection of phosphorus (P), iron (Fe), and aluminum (Al) in the fractions. Additionally, the dissolved organic matter (DOM) content was derived from the online UV signal. Two distinct fractions were detected and characterized. For the first size fraction, variations in P concentrations strongly correlated to the course of Al variations; in addition, high Fe presence in both fractions was accompanied by high P concentrations. Moreover, DOM was detected with P in presence of Fe and Al. Possibly, Fe and Al containing particles are carriers of P compounds and associated with organic matter. The study enables for the first time to trace and conceptually define the inputs and source regions of fine colloidal and nanoparticulate fractions within a small river of a headwater catchment. The stream water investigations will be extended to additional test sites and a broader range of elements.

Interaction of pesticides with some manganese-organic molecules based frameworks

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Particular chemicals like pesticides which use, in agriculture, became inescapable are engendering an environmental pollution and more particularly that of the waters as well of surfaces as ground-water sheets. It is urgent, for preservation of public health, to reduce at most our exposure to these substances and to operate everything to reduce and control these pollutants.

So, the presence of pesticides in drinkable waters is severely regulated and the producing companies of water, to conform to the established standards, are obliged to include in their networks of water treatment, processes to eliminate them.

The adsorption on the synthetized metal organic complexes may be a technique to disinfect waters polluted by pesticides and other chemicals.

In this context, some coordination compouds of manganese were tested in the adsorption of mitrobuzin present in contaminated water. The retained organic molecules are natural products (flavonoids and purines)

The preliminary results seems encouraging and we report them here. They are compared to those obtained with a conventional adsorbing agent, namely powdered activated carbon F400.

Speciation of phosphorus and colloidal Fe and Al (hydr)oxide complexes in particle size fractions of an arable soil

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Soil organic and inorganic phosphorus are in the majority of cases stabilized through the association with mineral components, especially with Fe and Al (hydr)oxides. However, few studies have focused on the relative contributions of different organic and inorganic forms of P bound to Fe and Al oxide colloids. In our arable soil study, amorphous and crystalline minerals were separated by selective dissolution with oxalate acid and dithionite–citrate from various particle-size fractions (>2000, 450-2000, 100-450, and 1-100 nm). Asymmetric flow field-flow fractionation (AF4) coupled to inductively coupled plasma mass spectrometer (ICP-MS), solution ^{31}P-nuclear magnetic resonance spectroscopy (NMR) and transmission electron microscopy (TEM) were employed. They were used to examine the speciation and contribution of (inorganic and organic) P bound to amorphous and crystalline Fe and Al (hydr)oxides in several soil fractions and to study the mechanism behind P fixation to these colloids in arable soil.

Results showed that colloids and nanoparticles have higher amounts of Fe, Al and P than larger sized particles. P is, to a large extent, associated with amorphous Fe and Al (hydr)oxides. Soil nanoparticles <100nm revealed two size fractions measured by AF4. The smaller size fractions (below 5nm) consist of natural organic matter (NOM) with a high UV-absorbance and P content. The larger size fraction (approximately 60nm) is a complex of Fe and Al (hydr)oxides linked to P, clays and NOM. Furthermore, it is more likely that the P absorbed to NOM is bound to crystalline rather than to amorphous Fe and Al (hydr)oxides.

Electroosmotic intensification of pressure driven dewatering of FINE CLAY SLUDGE

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Dewatering of disperse systems is an important problem for consolidation of sludge occurring in treatment of waste and drinking water, as well as for mining, food, paper, pharmaceutical and other industries. The most used methods include thermal drying, pressure and vacuum filtration, centrifugation and other mechanical methods. However, thermal methods need high power consumption and efficiency of mechanical methods goes down when handling fine materials characterized by small particle sizes and low hydrodynamic permeability (gel sewage sludge, different clayey waste, etc.). One of the ways to enhance the mechanical methods is the use of combination of pressure driven dewatering with electroosmotic one, for which the hydrodynamic permeability of the material is not a critical parameter, and the power consumption is much smaller comparing with the thermal methods. At such combination of dewatering factors the applied pressure not only squeezes the water, but also provides the contact of electrodes with partially dewatered sludge preventing the rupture of electric circuit and, correspondingly, the cessation of electroosmotic flow.

Efficiency of combination of pressure driven and electroosmotic dewatering is determined by combination of two opposite factors. Firstly, to promote the compaction of sludge under action of pressure the electrostatic repulsion between the particles must be decreased, that is possible at the reduction of the surface potential. Secondly, it is necessary to enhance the electroosmotic velocity of liquid flow through the sludge, i.e. to enlarge the surface potential of disperse particles. Since we have two contradictory conditions, the optimization of dewatering process is rather complicated task, which requires a careful control and regulation of the characteristics of particles and pore solution, and optimization of parameters of sludge treatment.

The experimental investigations of the conditions necessary for enhancement of pressure driven dewatering were conducted using a model system based on the dispersion of kaolinite, which is fine clay material. Since electrokinetic potential and, correspondingly, the velocity of electroosmosis depend on the equilibrium pH of pore solution, we performed detailed analysis of dispersion properties at different concentration of acid or alkali solutions introduced in the used dispersion. Particularly the magnitude and sign of the zeta potential of disperse particles and the velocity of electroosmotic flow at different values of pH were studied. In result of these investigations a sufficiently wide range of pore solution pH ($9<pH<12$), wherein the electrokinetic potential of the kaolinite particles and the electroosmotic velocity of liquid through kaolinite dispersion remain almost constant, was found. It is important to stress that the optimal conditions for the electroosmotic component of dewatering depend not only on pH of introduced acid or alkali solutions, but also on the equilibrium values of pH, which is defined by the buffer and ion-exchange capacities of the dispersion. Large values of pH, i.e. high concentration of electrolyte, corresponds to the case of relatively thin electrical double layer and, correspondingly, low energy barrier between the particles that should improve the compressibility of the dispersion, leading to the increase of the pressure driven component of dewatering.

The experimental investigations of dewatering efficacy were performed at a few initial moistures of dispersion, different values of applied pressure, voltage and treatment time. The main regularities of dispersion compression and dewatering were obtained that allow predicting the optimum conditions of sludge treatment.

Computational adsorption experiments with Materials Studio 5.0 compared to GIXRD-results: The influence of Fe- and S- defect sites on the adsorption model of H_2O at the (100)-pyrite surface.

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Chemical reactions at the (100)-pyrite (FeS_2) surface play an important role in many environmental, geological and chemical processes, e.g. acid mine drainage, bacterial pyrite oxidation, oxidation in aquifers and coal liquefaction and heterogeneous catalysis. During the last decades most studies about the pyrite surface structure and its adsorption properties were carried out in order to study reaction mechanisms and active sites involved in acid mine drainage processes. In this process the oxidation of pyrite leads to the formation of sulfuric acid that could be problematic for the ground water cycle. To understand these processes it is of essential importance to understand the adsorption properties of pyrite to organic molecules and water. The structures of the dry (100)-pyrite surface and the interface of the (100)-pyrite surface with water were determined with grazing incidence X-ray diffraction experiments (GIXRD) previously[1,2]. An adsorption model for water at the pyrite surface was determined including three adsorption layers, a transitional zone of partial ordered water molecules and water molecules that occupy defect sites of the topmost FeS_2-layer.

In this study the adsorption model of water at the (100)-pyrite surface near iron and sulphur defect sites is analysed and compared to experimental results. We present computational experiments, especially molecular dynamic simulations using the forcefield COMPASS. The simulations were carried out with the program package Materials Studio 5.0, particularly the program “Forcite”, from Accelrys Inc. The surface cell structure determined previously from GIXRD experimental results was used as a start model for the simulations. A surface area of 3x3 surface cells (16,25Å^2) and a depth of 2,5 surface cells (13,5Å) of pyrite was selected for the simulations. A vacuum slab of 30Å was added as adsorption region to permit enough mobility of the H_2O-molecules during the dynamic runs. Different amounts of iron and sulphur defect sites were introduced to the topmost FeS_2-layers of the surface during different simulation runs. Each dynamic run was calculated for 200ps with a step width of 0.2fs. The geometry optimization includes the smart method, using the Ewald-summation method for electrostatic and the atom based calculation method for van-der-Waals interactions.

The introduction of sulphur defects to the surface model has a stronger influence to the H_2O-adsorption model compared to the effect of iron defect sites. By introducing iron defects the adsorption model shows no differences compared to a surface free of defects. Only partially a small decrease in the distance between the topmost FeS_2-layer and the first H_2O-adsorption layer about 0.2-0.4Å was determined. The sulphur defects show a stronger influence, as H_2O-molecules could be observed in the topmost FeS_2-layers occupying the defect sites of sulphur dimers. Additional adsorbed H_2O-molecules occur between the topmost FeS_2-layer and the first H_2O-adsorption layer that is located 2.0(3)Å above the topmost FeS_2-layer. These results are in good agreement with the previously determined experimental model from GIXRD-data, with molecular dynamic simulations after Philpott et al.[3] and UHV-experiments carried out by Guevremont et al.[4].

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Characterising silver nanoparticle stability in suboxic waters

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Manufactured silver nanoparticles (AgNPs) are released into the aquatic environment from a range of waste water from domestic, medical, industrial and manufacturing sources. The presence of colloidal Ag in environmental samples has been known for some time, but has not been effectively characterised. Recent studies have investigated in detail the impact of critical environmental parameters such as pH, elemental composition, ionic strength and particle properties such as capping agents (AgNP stabilisers) on the behaviour of AgNP in idealised solutions and bacterial growth media.

The potential for the formation of AgNPs via reduction of Ag^+ ions in the presence of humic acids (HA) has been indicated in recent reports. Redox conditions play an important role in the stability of environmental AgNPs; following contact with dissolved oxygen in water, AgNPs can degrade over time and release $Ag^+(aq)$ ions; these may form AgCl particles, which in turn may agglomerate or be reduced back to AgNPs. Sulfidation also strongly affects surface properties of AgNPs, modifying surface charge and dissolution rate. There is a common assumption that these are very stable and low in toxicity, however there is limited experimental data to support this at present.

To date, very few studies have characterised AgNPs in suboxic environmental matrices using multiple techniques or investigated their fate/stability in realistic environmental matrices/AgNP concentrations. Using Dynamic Light Scattering (DLS), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and zeta potential, we have characterised citrate- and PVP-capped AgNPs in a suboxic matrix to explore the effects of humic substances and S^{2-} on AgNP. Initial findings suggest that the kinetics of humic-AgNP interactions are rapid and that the PVP-capped AgNPs show minimal interaction with the sulphide or HA. This contrasts with the behaviour of citrate-capped AgNPs where changes in particle size distributions have been observed (Figure 1). Further investigations of these effects are in progress.

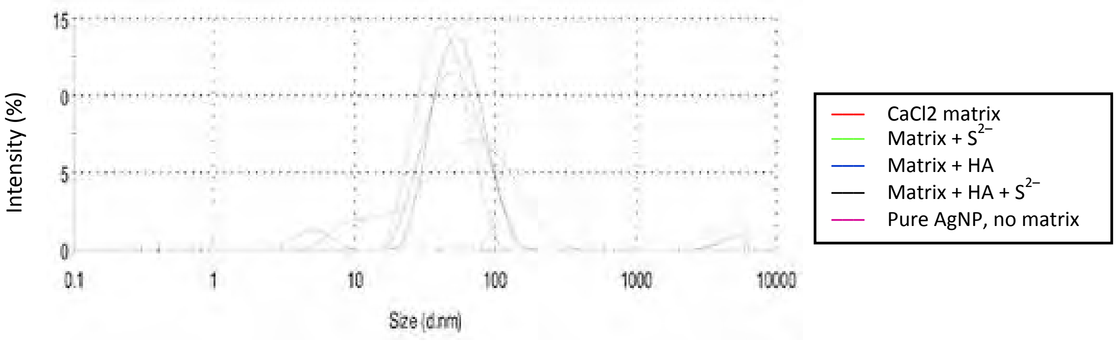

Figure 1 Observed DLS size distributions for citrate-capped AgNPs in presence/absence of HA and S^{2-}.

On the role of colloids and nanoparticles for the distribution of phosphorus in a forest topsoil

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Colloids and nanoparticles play an important role for the binding, transport and distribution of nutrients like phosphorus in soil. High percentage of total phosphorus contents are associated to inorganic and organic fine colloids < 450 nm but their relevance is often neglected within this soil fraction. In forest soil, P is accumulated in surface and upper mineral layers but the lateral distribution of P in topsoil is highly inhomogeneous.

In this study samples from a coniferous forest were taken along a 2 m x 0.5 m grid with 30% slope. The effect of the slope position on the phosphorus distribution in the acidic topsoil samples was investigated. Water dispersible colloids (WDC), which represent the transportable colloid fraction, were extracted from field moist soil samples. Different size ranges (≤ 1µm, ≤ 450 nm, ≤ 100 nm) of WDC were separated and analyzed. The Field Flow Fractionation technique coupled online to UV-, DLS- detector and inductively coupled plasma mass spectrometry (ICP-MS) enabled a size resolved characterization of the colloidal fraction < 450 nm and their elemental composition (Fe, Al, P, Ca, Mn).

Colloids of surface- and mineral soil layers differed in colloidal composition and size distribution. Both layers show differences regarding particle bound phosphorus concentrations between the size range of 100 and 450 nm. The total phosphorus content does not correlate with slope whereby the colloidal bound phosphorus content increases with it.

The results confirm that P associated to colloids can be laterally translocated in soil and might be responsible for the heterogeneous distribution of P in the topsoil layers. Differences in size-dependent phosphorus amounts indicate a preferential association of P to distinct colloid forms. To characterize the organic P species liquid ^{31}P-NMR measurements will be performed.

Interaction of polyacrylamide flocculants and acrylamide with clays, soil and sediments

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Polyacrylamide flocculants are used in numerous fields, particularly for water treatment and offshore oil production. These polyacrylamide polymers, with an ultra-high molecular weight, are produced from acrylamide monomer, which is known to be an animal and a suspected human carcinogen. The fate and transport of acrylamide and polyacrylamide flocculants in the environment in the above contexts have never been studied yet. In this study, we were interested in acrylamide and 2 anionic polyacrylamides of different molecular weight: the first one is used as flocculent in an aggregates quarry, and the second one is used in offshore oil extraction. For both acrylamide and polyacrylamides, batch experiments (sorption isotherms) according to the protocol developed by the Environmental Protection Agency (EPA) [1] were conducted on mineral soil phases, soil materials and sediments to determine the partition coefficient between the solid and the liquid phase (Kd), and to provide a better understanding of these molecules fate when they are in contact with natural solid phases. For acrylamide and the polyacrylamide used in the aggregates quarry, the tests were performed in freshwater with clays and sludge from one quarry site. For polyacrylamide used in petrochemical, experiments were carried out in sea water with clays and marine sediments.

Figure 1 presents the adsorption isotherms obtained for acrylamide in contact with kaolinite, illite and a sluge collected in the quarry. The results from figure 1 indicate a weak affinity of acrylamide to clays and to soil samples (Kd < 0.9 ml/g). These results are consistent with those of Arrowood (2007) [2] who found low adsorption percentages (0-2.4%) of acrylamide on three soil types. This low affinity can be explained by the high solubility and hydrophilicity of acrylamide, its small size and the negative charges of both acrylamide and the surfaces of solids tested, as shown by zeta potential analyzes. Acrylamide is mobile in the soil since it cannot be trapped by mineral particles. Unlike the acrylamide, the two polyacrylamides tested showed a strong affinity to clays, sludge and sediments.

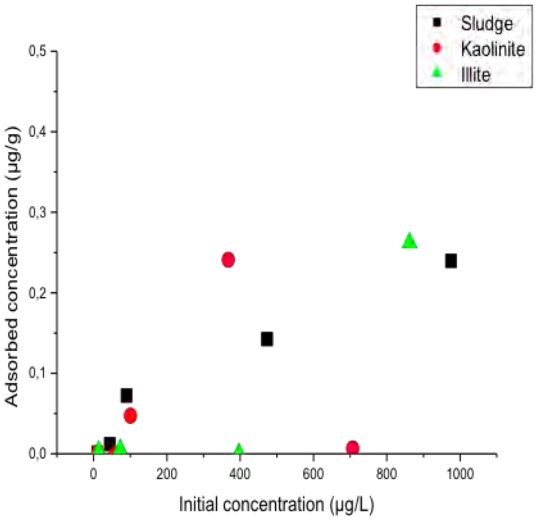

Figure 1 Adsorption isotherms of acrylamide onto two clays (Kaolinite, Illite) and sludge from the aggregates quarry, with solid/liquid ratio= 200 g/L, I= 10^{-3}mol.L^{-1} at pH=7.0

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Synthesis and characterization of magnetite/clay composites

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Nowadays, the receipt and investigation of different properties of magnetite/clay composites is one of the most rapidly developing areas of modern nanoscience. Magnetic materials known to mankind for a long period, and it is well known, what kond of the role played by the magnetic phenomena in human life. However, searching for data on the preparation and characteristics of magnetic composites showed that these composites is very little studied. In connection with this research objective was synthesis of magnetite/montmorillonite and magnetite/kaolinite composites and study their different properties.

In this work were synthesized magnetite/montmorillonite and magnetite/kaolinite composites of sequential treatment with salts of iron (II) and (III).

Magnetic properties and phase analysis of these composites were characterized by vibration sample magnetometry and XRD analysis. Vibration sample magnetometry results were showed themselves above the clay minerals have magnetic properties in native form, a fact confirmed by the absence of a magnetic hysteresis for them. The resulting composites are shown based on their magnetic properties and responsive to an applied magnetic field. Depending on the availability of iron oxide particles in the inter-packet space of montmorillonite and kaolinite minerals has the phenomenon of magnetic hysteresis. As the concentration of magnetite in the composites magnetization increases to a maximum value (27.6 emu/g and 31.6 emu/g), typical for magnetite/montmorillonite and magnetite/kaolinite composites, respectively. Magnetization values of the magnetite/montmorillonite and magnetite/kaolinite composites are comparable with the magnetization value of magnetite, which is associated with the state of nanoscale magnetite particles in the composite structure of clays.

Were synthesized magnetite/montmorillonite and magnetite/kaolinite composites, and with the inclusion of particles of magnetite in the structure of these minerals is proved by XRD and SEM. The results of these methods was also demonstrated the presence of magnetite phase in all the samples. Based on these results it is concluded that synthesizing magnetite/montmorillonite and magnetite/kaolinite composites can achieve high rates of their magnetic properties. The concentration of magnetite in the composites will be relatively is low.

Interaction of Some Peticides with Iron Organometallic Compounds

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Particular chemicals like pesticides which use, in agriculture, became inescapable are engendering an environmental pollution and more particularly that of soils.
It is urgent, for preservation of public health, to reduce at most our exposure to these substances and to operate everything to reduce and control these pollutants. Some conventional adsorbing product such carbon F400 are frequently used.

The adsorption on the synthetized metal organic complexes may be a alternate technique to disinfect soils and waters polluted by pesticides and other chemicals.
In this context, some coordination compouds of iron were tested in the adsorption of mitrobuzin present in contaminated water. The retained organic molecules are natural products (flavonoids).

The preliminary results seems encouraging and we report them here.

Retention of ionic pesticides at the soil–solution interface

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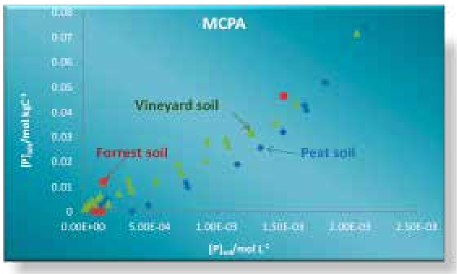
Soil constitutes are an organized system that comprises different organic and mineral components. Its surface acts as a complex geochemical interface that establishes a boundary between soil and soil solution. Pesticides are a class of persistent organic pollutants that play an important role in crop production and protection. Among pesticides, we can find compounds with a big variety of chemical formulations that can have adverse effects on human health and persist in the environment due to its high affinity for soil organic matter, especially for humic substances. This affinity will be affected by the nature of the organic matter and by the type of pesticide and will affect itself the transport, bioavailability and persistence of these substances in the environment (Roldán et al., 2011, *Anal Chim Acta*, 699, 87–95).

The objective of this study is to obtain information of the adsorption process of pesticides in soils in order to be able to predict and control its fate in the environment. The retention of ionic pesticides paraquat and MCPA by different soils (peat soil, forrest soil and vineyard soil) has been analyzed. This retention capacity of the soils can be interpreted as a function of some factors such as pH, ionic strength or the organic matter content. The results will confirm that the organic and the mineral fraction of soils can contribute differently to the behavior of pesticides in soils and depending on the dominant phase experimental adsorption data can be normalized for the organic carbon content (see figure).



Adsorption of Anionic Surfactant on Silica

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Introduction: Surfactants are widely used in many fields which are closely related to our life and environment. Large amount of studies were reported during the past several decades about the adsorption of cationic surfactant on silica and anionic polymers, when it comes to anionic surfactant on silica, there is only few researches upon it, in this research, sodium dodecyl sulfate (SDS) adsorption on silica was investigated under different pH (3, 5 and 7) and NaCl concentration (0.1, 100mmol/L).

Materials and Methods: Quartz silica of 1.2 µm in average diameter was purchased from Sigma-Aldrich. SDS with linear alkyl chain was used. A batch method was taken to obtain the adsorption amount of surfactants. Surfactant concentration was measured by surfactant selective membrane electrode method. Adsorption isotherms were fitted with both Langmuir and Frumkin–Fowler–Guggenheim (FFG) equation.

Result and Discussion: In 0.1mmol/L NaCl solution, whatever pH performed, the concentration of surfactant after equilibrium kept, infinitesimal changes happened, no binding was found. At lower NaCl concentration, SDS adsorption can hardly happen because the screening effect of Na^+ decreased and the electric repulsive force became larger.

In 100mmol/L NaCl solution, as the figure shows, a sharp increase as the first stage of adsorption isotherm was observed. The slope of adsorption isotherms showed larger than unit in double logarithmic scale. When the slope is unit, it is the so called “Henry slope”, which indicates the adsorption on isolated “equal energy” site that follows the ideal adsorption of the Langmuir equation. The steeper slope indicated a cooperative adsorption which was caused by the hydrophobic interaction among the adsorbed SDS ions. SDS adsorption became stronger by gathering together, FFG equation was better fitted. The second stage showed a Langmuir-increase and a pseudo plateau formatted when it was the third stage.

The adsorption at lower pH was larger than that at higher pH because the negative charge of the silica increased with increasing pH and the increase of the negative charge induced the increase of repulsive force between SDS and the silica.

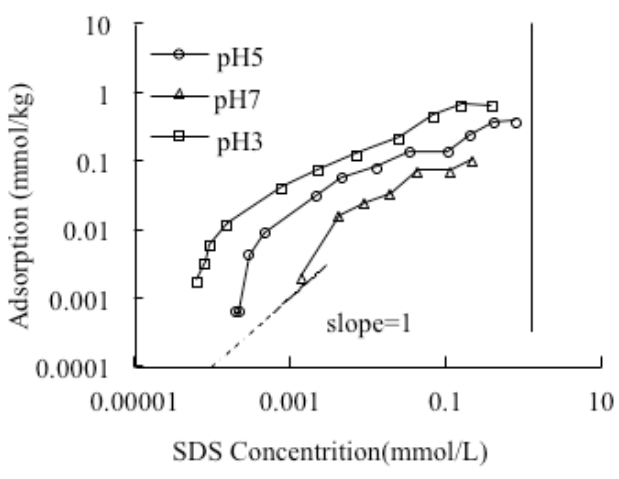

Figure 1 Adsorption isotherms of different pH and NaCl concentration conditions

Adsorption characteristics of anionic surfactant and anionic dye onto alpha alumina with small surface area

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We investigated adsorption of anionic surfactant sodium dodecyl sulfate (SDS) and anionic dye new coccine (NC) onto α-Al_2O_3 with low surface area as a function of pH and NaCl concentration. Figure 1 shows that the SDS adsorption isotherms () onto α-Al_2O_3 as a function of NaCl concentration at pH 4 has a common intersection point (CIP) corresponding to surface charge neutralization [1]. The CIPs were also observed at pH 5 and pH 6. The SDS adsorption decreases with increasing electrolyte concentrations below CIP. Nevertheless, above CIP the salt effect is reversed so that the adsorption density reduces at lower ionic strength. In Figure 2, the adsorption isotherms of new coccine () onto α-Al_2O_3 at pH 4 are indicated as a function of NaCl concentration. The increase in the ionic strength decreases the maximum dye adsorption density. The trend is different with surfactant adsorption. Furthermore, the maximum adsorption of both SDS and NC onto α-Al_2O_3 increases with decreasing pH (data is not shown) because of the increase in positive surface charge. While the change in pH upon SDS adsorption onto α-Al_2O_3 was observed, this change was not significant for NC adsorption.

The calculated curves from 2-step adsorption model can reasonably represent experimental results of SDS and NC adsorption isotherms onto α-Al_2O_3 at different salt concentrations (solid lines in Figure 1 and 2), suggesting that the adsorption of SDS and NC onto α-Al_2O_3 should be described by a multilayer adsorption than monolayer adsorption isotherms [2]. The maximum SDS adsorption density was much higher than NC adsorption density, demonstrating the presence of hemimicelles or admicelles in the surfactant adsorption.

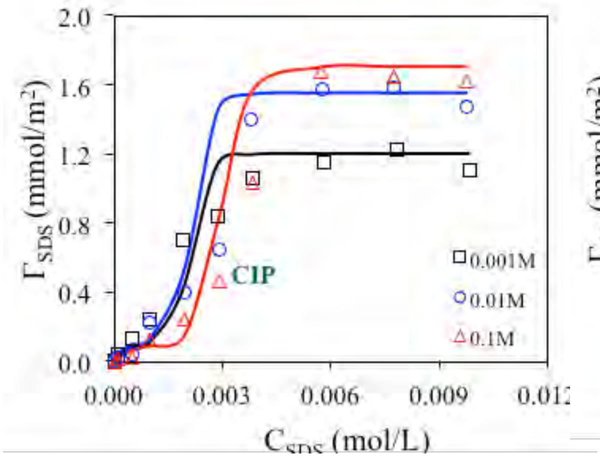

Figure 1 Adsorption isotherms of SDS onto α-Al_2O_3 as a function of NaCl concentration at pH 4.

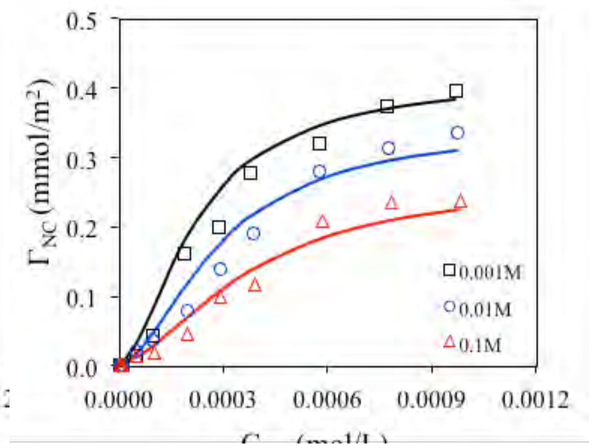

Figure 2 Adsorption isotherms of NC onto α-Al_2O_3 as a function of NaCl concentration at pH 4.

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Performance of ionic MOFs on the capture of radionucleides

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Recently, some crystalline hybrid porous solids known as Metal Organic Frameworks (MOFs) emerged as promising systems for gas adsorption and drug encapsulation.[1] Indeed these hybrid solids, constituted by inorganic nodes (metal chains or clusters) linked each other by organic linkers, present a large specific surface area and pore volumes as well as a high chemical versatility allowing to modulate the chemical and physical properties indefinitely.

Even if few results are available in the literature, the adsorption by such solids possessing extra-framework ions could be evidenced as a plausible, economic and simple solution to eliminate toxic contaminants in water.[2] Various parameters can influence the ability for sorption of porous solids such as the charge of the framework, the adsorption interaction and the diffusion in the pores.[3]

For this study, we have followed a strategy combining experimental techniques (adsorption calorimetry and isotherm, X-ray Diffraction) with computational approach (Molecular Dynamics) to elucidate both the microscopic mechanisms in parallel of the macroscopic behavior allowing us to rationalize the ion exchange process for both I^- anion and Sr^{2+} cation in MOFs containing extra-framework ions. Further, one anionic and one cationic MOF have been chosen for this study, in which the impact of the topology and the framework charge is discussed on the ionic exchange properties, i.e. the adsorbed ion quantity as well as the adsorption energy. We have clearly evidenced the high adsorption capacity of the materials studied. This allows the potential use of such innovative materials for decontamination process to be envisaged.

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Dye adsorption at the TiO_2/water interface and correlation with photocatalytic degradation

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In numerous studies of photocatalytic degradation of organic pollutants, the main emphasis is usually placed on the modification and fine-tuning of the catalyst surface properties to improve their photocatalytic efficiency under UV or Visible radiation. Much less attention is paid to the pollutant adsorption stage, which is a pre-requisite for the ultimate photocatalytic reactions. Such characteristics of the adsorbed pollutant species as the strength and reversibility of their adsorption on the catalyst surface or their orientation and concentration within the interfacial region may certainly affect the performance of the photocatalytic process. There is thus an urgent need for systematic studies of the underlying adsorption mechanisms.

The main interest of the present preliminary study was to establish the relationship between the dye adsorption capacity of several powdered TiO_2 samples, varying in particle size and morphology, and their efficiency in photocatalytic dye degradation from aqueous solutions. For this purpose, Rhodamine 6G was adsorbed from aqueous solution under various dye concentration, pH, and ionic strength conditions. The following TiO2 samples were used as solid adsorbents (the crystalline composition, as determined based on XRD measurements, is given in brackets): nanocrystalline anatase (100% anatase), P-25 Degussa (80% anatase, 20% rutile), nanofibers synthesized using electrospinning method (68-75% anatase, 32-25% rutile), as well as a series H nanotubes containing as-made, freshly calcined or calcined and aged samples. These materials were characterised by nitrogen gas adsorption and electrophoretic measurements to know their specific surface area and surface density of electric charge under different experimental conditions. Then the adsorption isotherms for Rhodamine 6G from aqueous solutions were determined by means of solution depletion technique. Finally, the photobleaching and photocatalytic performance of the TiO2 samples was tested under free pH and ionic strength conditions. The first conclusions drawn from this work should certainly be useful in view of further optimisation of the overall photocatalytic treatment for organic pollutant degradation.

Analysis of surface of the titanium electrode after precipitation of indium

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Abstract: Electrochemical characteristics of deposition and dissolution of indium in chloride solutions using the method of cyclic voltammetry were determined. The effect of the polarization of the interval and scan rate at electrochemical reactions which occur in the system was studied. Electron microscopy observations and X-ray diffraction patterns confirmed the formation of crystalline indium deposits.

Keywords: indium, discharge-ionization, current density, scan rate, electrode process, potential

Currently, there is increasing interest to the problem of obtaining high-purity indium /1/. This work is a continuation of studies of electrochemical behavior of In^{3+} on platinum and titanium electrodes to find effective ways of cleaning rough indium /2/. Methods of scanning electron microscopy and X-ray diffraction analysis used in this work have revealed the presence of cathodic precipitated metallic indium on the surface of the titanium electrode and helped to find optimal conditions of the processes studied. Chronoamperograms of studies carried out were obtained to study the effect of electrolyte concentration, potential and electrolysis time on the precipitation and dissolution of indium. Variation of potentials interval revealed the potential of total precipitation of indium on the surface of titanium electrode, which amounted to -1.1 V. This result was obtained on the basis of X-ray diffraction analysis and scanning electron microscopy of surface of samples of titanium electrode coated with metallic indium. Changing the concentration of indium in the solution has a strong influence on the rate of recovery of indium. Analysis of the electrode surface after polarization at different concentrations of indium in the solution (0.1 M) revealed an optimal concentration of 0.5 M, when there is a maximum recovery rate of indium. Furthermore, the results of scanning electron microscopy showed that the best precipitation for all three concentrations occurs at the potential of -1.1 V. During the electrolysis of 0.5 M sodium chloride solution, indium (E_e = -1.1 V), the formation of coarse sediments of indium on titanium surface is observed. Carrying out the electrolysis at potentials of -0.8 V and -1.3 V results in the formation of non-uniform precipitation of amorphous indium. Apparently at -0.8 V only beginning of precipitation of indium is observed, and at -1.3 V the recovery of hydrogen occurs, complicating the process of precipitation of indium. Indium precipitations obtained in these experiments were analyzed by XRD method.

Experiments on the effect of electrolysis time were carried out for a detailed investigation of indium precipitation process on the surface of titanium. The amount of precipitated indium and crystals become larger with the increase of electrolysis time.

Chronoamperograms of indium precipitation and dissolution at potentials of E = -1.1 V for the cathodic process and E = -0.5 V and E = 0.2 V for the anode were obtained to identify the potential of indium ionization on titanium electrode surface. It is obvious from the results of X-ray diffraction analysis and scanning electron microscopy that the shift of dissolution potential in the anodic region leads to an increase in the rate of oxidation of indium.

Thus the results of presented work can be used in the development of electrochemical method of indium refining.

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Potential of electrokinetic process for the remediation of estrogens in soil

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Some organic contaminants can accumulate in organisms and cause irreversible damages in biological systems through direct or indirect toxic effects. In this study, the feasibility of electrokinetic process (EK) for the remediation of estrogens 17β-estradiol (E2) and 17α-ethynyl-estradiol (EE2) was studied in a stationary laboratory cell. Both compounds are defined as “emerging” contaminants and are known to be endocrine disrupting agents.

Two soils were used in this study: S1 (Valadares, Vale de Milhaços, 0–15cm depth) and S2 (Paul de Magos, Salvaterra de Magos, Portugal, 0–20 cm depth). Soil S1 (sandy) was used as a support medium and S2 (silty loam) as the contaminated matrix. Four experiments were carried out without pH control at 0, 10 and 20 mA; and with pH control (anolyte, pH > 13) at 10 mA.

The analysis of the soil section near the anode and cathode end for all experiments showed that all the contaminants were remediated during the experiment although at different extents. Electroosmotic flow towards the cathode end was the mechanism responsible for the contaminants mobilization, being more expressive when pH was controlled. Estrogens presented slightly different behaviours during EK. When 10 mA were applied 39 % of E2 and 50 % of EE2 remained in S2. When 20 mA were applied the remediation only 30 and 35 % of EE2 and E2, respectively remained in S2. Between 44 to 69 % of the compounds were degraded mainly due to the formation of ·OH radicals.

Remediation of organic contaminants seems to be feasible through an integrated approach with different remediation/removal mechanisms (EK transport, electro- and photodegradation).

The results here presented are of valuable knowledge for the remediation of organic contaminants using the EK process.

Keywords: *Electrokinetic remediation, electroosmotic flow, electrodegradation, estrogens, soil*

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Potential of salt marsh plants for the remediation of organic compounds

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To assess the potential of *Halimione portulacoides* and *Spartina maritima* for the removal of caffeine (Caff), 2-hydroxy-4- methoxybenzophenone (MBPH) and triclosan (TCS) from aquatic medium, a 10-day experiment was carried out. At laboratory conditions, plants were exposed to 1 ppm of each contaminant in sediment elutriate and in sediment soaked in elutriate. Sediment, water and plants (with same age and size) were collected in Tejo River estuary, Portugal. Target contaminants were analyzed in liquid (solid phase extraction) and solid samples (ultrasonic extraction) and determined by gas chromatography coupled with flame ionization detector. Chlorophylls and carotenoid contents were assessed and suggested no significant deletory effects resulting from the 10-days exposure to these organic contaminants at this concentration. Preliminary results suggest that remediation was achieved by different removal mechanisms including photodegration and biological mechanisms. Results will be presented and discussed in the scope of the suitability for a field scale remediation set-up.

Keywords: *salt marsh plants, caffeine, 2-hydroxy-4- methoxybenzophenone, triclosan, sediment elutriate*

Acknowledgements

Financial support was provided by FP7-PEOPLE-2010-IRSES-269289-*ELECTROACROSS - Electrokinetics across disciplines and continents: an integrated approach to finding new strategies for sustainable development*, PTDC/ECM/111860/2009 - *Electrokinetic treatment of sewage sludge* and *membrane concentrate: Phosphorus recovery and dewatering*. N. Couto acknowledges Fundação para a Ciência e a Tecnologia for Post-Doc fellowship (SFRH/BPD/81122/2011).

Effect of pH on adsorption of arsenic onto fly ash

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Arsenic in natural waters represents a serious health hazard. The chemical and biological weathering provide arsenic species to groundwaters [1]. High arsenic concentrations have been reported recently from Chile, Argentina, India, Bangladesh, China, Taiwan, USA, Canada, Hungary and Poland [2,3]. Drinking water having arsenic beyond permissible limit is dangerous for people life. It causes skin, lung, bladder and kidney cancer as well as pigmentation changes, skin thickening, neurological disorders, loss of appetite and nausea [4]. Adsorption is a method frequently used for the water purification with arsenic [3].

In the present study, fly ash is used as adsorbent for removal of arsenic(III) in aqueous solution. Fly ash was obtained from burning brown coal and biomass from the power plant in Zgierz (Poland). The objective of this study was to compare arsenic(III) removal at natural pH (imposed by fly ash; pH 8.5) with the arsenic(III) adsorption at high alkaline (pH 12.5). The effect of adsorbent dose, temperature and contact time was investigated.

The maximum static uptakes of arsenic(III) by fly ash at natural and high alkaline pH were achieved for adsorbent-to-arsenic ratios of 20 g/L and was 14 $mg_{As(III)}/g_{sorbent}$ and 30 g/L and was 20 $mg_{As(III)}/g_{sorbent}$, respectively. Adsorption data of arsenic(III) onto fly ash were analyzed using Langmuir and Freundlich models. Thermodynamic parameters for the adsorption process were determined at 25 ^{o}C, 35 ^{o}C and 45 ^{o}C. The calculated values showed that arsenic(III) adsorption (both at natural and high alkaline pH) is a spontaneous and endothermic process. The process kinetics was evaluated by pseudo-first, pseudo-second order and parabolic diffusion models. Pseudo-second order model exhibited the highest correlation with experimental data (R^2 = 0.999). These results shows that the fly ash could be considered as potential adsorbent for removal of arsenic(III) ions in aqueous solution, at both natural and high alkaline pH.

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Removal of hypophosphite ions from water using ultrasound

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Hypophosphite ion ($H_2PO_2^-$) is well known as a reducing agent for electroless plating and as hydrogen donor in catalytic hydrogenation of organic molecules. On the other hand, the plating waste solution after electroless plaiting contains excess metal ions, $H_2PO_2^-$ and ligands that would cause serious contamination if not removed before discharge. Thus, many methods have been developed for removal, recovery and recycling of metal ions, $H_2PO_2^-$ and ligands from the plating waste solution. For example, $H_2PO_2^-$ is removed and recovered as calcium phosphate formed through the reaction of phosphite ions (HPO_3^{2-}) and phosphate (PO_4^{3-}) with calcium ions (Ca^{2+}). This means that $H_2PO_2^-$ must be oxidized to form HPO_3^{2-} and PO_4^{3-} for removal and recovery of $H_2PO_2^-$ from water. Fenton reaction is one of the routes for oxidation of $H_2PO_2^-$ to form HPO_3^{2-} and PO_4^{3-}, in which hydroxyl radicals (·OH) act as an oxidizing agent for $H_2PO_2^-$. Then, in this work, the ultrasound is applied for removal, recovery and recycling of $H_2PO_2^-$ from water because $H_2PO_2^-$ should be oxidized by ·OH generated from sonolysis of water ($H_2O \rightarrow H\cdot + \cdot OH$). In particular, we examined the effect of sonication time, ultrasound frequency, temperature, and solution pH on the sonochemical oxidation of $H_2PO_2^-$ and the resulting HPO_3^{2-} and PO_4^{3-}. We found that the amount of $H_2PO_2^-$ oxidized and the resulting HPO_3^{2-} and PO_4^{3-} increased with longer sonication time and higher frequency of ultrasound. On the other hand, temperature and solution pH did not affect the oxidation of $H_2PO_2^-$. Furthermore, we revealed that the oxidation of $H_2PO_2^-$ was enhanced with the addition of hydrogen peroxide (H_2O_2) water and titanium dioxide (TiO_2) powder. The oxidation of $H_2PO_2^-$ was also enhanced by introducing oxygen (O_2) gas into the hypophosphite solutions. Note here that the oxidation of $H_2PO_2^-$ was not observed in the absence of ultrasonication even if H_2O_2 water and TiO_2 powder were added and O_2 gas was introduced. This indicates that the oxidation of $H_2PO_2^-$ and generation of HPO_3^{2-} and PO_4^{3-} were enhanced by combination of ultrasonication with H_2O_2, TiO_2 and O_2.

Hydrodynamic behavior of Zero-valent Iron Permeable Reactive Barriers: Effects of Permeability Loss

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The permeable reactive barrier (PRB) is a widely used technology for in-situ subsurface remediation as it is capable of treating large contaminant plumes cost effectively. Zero-valent iron (ZVI) is a reactive material that has been extensively used as it is highly reactive and suitable for treating various kinds of contaminants, i.e. hydrocarbons and heavy metals. Despite the facts that ZVI-PRB has been used in groundwater remediation technologies, the complex mechanisms that occur in the treatment process need further studies and the longevity of the system is unpredictable. The significant issues that need to be addressed which is intimately related to the hydrodynamic of PRB is the rate of mineral precipitation and permeability/porosity reduction within the PRB as well as the potential of ZVI-PRBs for remediation of contaminants. A series of column experiments has been set up (14 cm inner diameter and length of 90 cm) and operated with the conditions imitating the natural groundwater environment, i.e. flow rate and water constituents. The experimentally measured values of main parameters following Darcy's law will be used in calculating the permeability and computer simulation. The corroded ZVI will be analysed to identify the composition of the precipitates and to determine the porosity changes using micro X-ray CT scanner (µCT) and X-ray Diffraction (XRD). From the flow column experiment, it can be seen that there is a drop in flow rate and a decrease in the intrinsic permeability relative to time, i.e. total flow. The XRD detected the chemical components of Magenetite and Maghemite which are the iron oxides that occur from the reduction of iron in water. The image from µCT indicated the changes in particle size, pore size and porosity. It can be concluded that the pores have been blocked due to the mineral precipitation thus reducing the flow rate and permeability. The results of the computer simulation can be used to determine the rate of mineral precipitation and support in designing the appropriate PRB, i.e. in term of longevity.

Keywords: Zero-valent iron, permeable reactive barrier, hydrodynamic, mineral precipitation

Protein complexation with Humic acids

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Humic substances (HS), including humic acids (HA) and fulvic acids (FA), are important components of soil systems. The reaction between enzymes and soluble humic matter has been attributed to co-polymerisation, adsorption and encapsulation of enzymes into the inner structure of humic matter. The importance of electrostatic and hydrophobic interactions between humic acids and proteins concluded that parameters like mixing ratio of HA and protein, pH and ionic strength determined the extent of HA-protein complexation and aggregation of the complexes. Complexation of oppositely charged HS and protein is a form of 'complex coacervation' or 'associative phase separation'. HS form strong complexes with oppositely charged proteins, which will lead to changes in the enzyme activity. The effect of soil HS on the activity and stability of two enzymes was investigated as a function of pH, ionic strength and mass ratio HS/enzyme. Humic acid (JGHA) and fulvic acid (JGFA) are negatively charged, lysozyme is net positive at pH values below 10.4 and urease is net positive below pH 5.2 or net negative above pH 5.2. The enzyme activities in the HS-enzyme complexes were suppressed when the enzymes were oppositely charged to the HS. The largest activity suppression was observed around the mass ratio HS/enzyme where the HS-protein complex was at its isoelectric point (IEP). At the IEP strong aggregation of the complexes led to encapsulation of the enzyme. The ionic strength was important; an increase decreased complex formation, but increased aggregation. Due to the larger hydrophobicity of JGHA than JGFA, the reduction in enzyme activity was stronger for JGHA. The enzyme stability decreased also maximally at mass ratio around the IEP of the complex when HS and protein were oppositely charged. When urease and HS were both negatively charged no complexes were formed, but the presence of JGHA or JGFA improved the activity and stability of the enzyme.

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Biocomposites on the base of yeast cells and diatomite such as sorbents of metal ions

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The problem of wastewater treatment is one of the most actual problems of modernity. Especially also extremely actual problem is cleaning wastewater of metallurgical industries from the metal ions. Natural minerals and synthetic ion-exchangers are widely used for remove the metal ions. Alternatively, they may serve as microorganism cells containing on its surface a different of functional groups like amine, carboxyl, hydroxyl, phosphate, sulfide, sulfhydryl, etc.

Were conducted experiments on the adsorption of ions Cu^{2+} and Pb^{2+} on the surface of yeast cells *Rhodotorula glutinis*. It has been shown that at the initial concentrations in the range of salts of Cu^{2+} and Pb^{2+} from 10^{-6} to 10^{-1} mol/l the removal degree of metal ions varies between (95.2 and 98.3)% to (50.1 and 59.7)% for ions Cu^{2+} and Pb^{2+}, respectively. In this case the adsorption equilibrium is reached after 30 minutes.

Method of IR spectroscopy shows that the interaction of yeast cells with ions Cu^{2+} and Pb^{2+} is realized by amino-, phosphate, carboxylic and hydroxyl groups of the surface, the ions Cu^{2+} are dominant donor-acceptor interaction with amino groups and ions Pb^{2+} - ion exchange with the phosphate and carboxyl groups. Due to the high lyophilic surface of cells their separation from solutions difficult. Therefore were carried out experiments to immobilize the cells Rhodotorula glutinis on the surface of natural mineral diatomite. Diatomite also has high sorption capacity with respect to the ions Cu^{2+} and Pb^{2+}, but does not provide complete water treatment. The removal degree of Cu^{2+} and Pb^{2+} ions by diatomite in the concentration range of their salts 10^{-5}-10^{-1} mol/l is (92.1-15.6)% for Cu^{2+} ions and (95.6-20.3)% for Pb^{2+} ions.

Experiments to immobilization of Rhodotorula glutinis cells showed that the attachment of cells to solid surfaces most efficiently at the surface of diatomite provisional modifications of polyethylenimine solution with a concentration of 0.03 base-mol/l. Modification of mineral surface with cationic polymer creates favorable conditions for attachment thereto of negatively charged cells of microorganisms. It is shown that by using the obtained composite biosorbent to remove of Cu^{2+} and Pb^{2+} ions from solutions the treatment degree of water is reaches 97.8-99.4 %.

Regulation of biodispersies stability by catonic polymers

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One of the factors limiting the widely use of cells of microorganisms in water treatment, is the difficulty of separating them from solutions. To solve this problem can be used flocculation of biological dispersion with polymers. Therefore we attempted to flocculation of yeast cells Sacharomyces cerevisae, algae and spherosome Shlorella vulgaris and plant cells spherosome by using cationic polymers like polyethyleneimine (PEI) and polydimethyldiallylammonium chloride (PDMDAAH).

Suspension of yeast cells and spherosome is fairly stable, the value of their optical density only slightly changed over time. Introduction of the suspension of yeast cells Sacharomyces cerevisae and algae Shlorella vulgaris solutions of PDMDAAH and PEI with concentration range 10^{-6}-10^{-1} base-mol/l leads to a substantial decrease in their optical density, and with increasing polymer concentration to increase the settling rate of the particles. This is due to flocculation of biodispersions in result of adsorption on them the polymer macromolecules.

Analysis of data on the aggregation of yeast cells, algae and spherosome of plant cells in the presence of PEI and PDMDAAH, change their electrokinetic potential, PEI adsorption on the surface of yeast cells suggests that along with flocculation by neutralization mechanism in these systems occurs due to aggregation on account of bridge formation. This is confirmed by experiments on the change of the reduced viscosity of the cell-PEI.

Calculation of the interaction energy of cells in the presence of polymers is difficult because of the complexity into account the specific adsorption of polymer macromolecules. On the cell surface interaction energy values Sacharomyces cerevisae cells in a medium of sodium chloride are high in a wide range of distances between the particles, the negative energy values are found only at distances greater than 6500Å. From this it follows that the flocculation of yeast cells with cationic polymers proceeds by a mechanism for further aggregation accompanied by the formation of the amorphous structure.

Decontamination of solution containing radioactive strontium by sodium nonatitante

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After using a combustible in nuclear reactor, this latter contains different radioactive elements, which do not represent an interest to produce energy. These elements are called fission products. One of them, which have a long half-life, is the strontium 90 (^{90}Sr). After the dissolution of the combustible in concentrated nitric acid, strontium is dispersed in an aqueous as a divalent ion Sr^{2+}. Thus, in order to reduce the volume of the wastes, strontium has to be concentrated, and the current dominant process is co-precipitation. However this process produces a lot of secondary wastes that need a special treatment. In order to reduce these secondary wastes, different processes have been studied and an interesting one is solid-liquid extraction. Different kinds of inorganic material have been proposed as extractants of strontium and one group emerges because it presents a high selectivity and a good radioactive stability: porous titanates. Among these materials, sodium nonatitanate, of chemical formula $Na_4Ti_9O_{20}$, xH_2O, has a good cationic exchange capacity [1] and it has been studied by several experimental and theoretical investigations.

As any oxide, the exchange capacity of sodium nonatitanate is function of the pH [2]. In order to minimize the influence of the pH on the adsorption of the strontium by the sodium nonatitanate, sodium acetate have been used as buffer. A solution containing strontium nitrate and sodium acetate has been used as a simulant of nuclear solution in order to model the adsorption of the strontium [3]. We show that the exchange is governed by nearest neighbours interactions in the solid phase [4]. The acidic constant has also been obtained thanks to the modelling of the adsorption rate as a function of the pH. Such general studies provide important relevant information for the design of the practical applications.

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One-step synthesis of δ-MnO_2 nanoparticles using ascorbic acid and their scavenging properties to Pb(II), Zn(II) and methylene blue

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As environmentally friendly materials, manganese dioxides with a layered structure (δ-MnO_2) display good adsorption properties to heavy metals (such as lead, zinc and copper) and dyes (such as methylene blue (MB) and Congo red); the latter also undergo oxidative degradation. δ-MnO_2 materials are usually prepared by redox reactions using a variety of methods that result in different surface areas, particle sizes and types and numbers of structural defects of the synthesized δ-MnO_2. At lower temperatures, the redox reaction is easier to control, and the SSA of obtained δ-MnO_2 is larger. Furthermore, the scavenging to heavy metals of δ-MnO_2 is much more superior.

Ascorbic acid (AA) as a strong organic reducing agent can reduce high-valence manganese efficiently under mild conditions to produce δ-MnO_2 with a large SSA. Under ice-water bath condition, at pH2 and pH3, well-crystalline layered δ-MnO_2 was formed (Figure 1). The SSAs of the S_{10-3} and S_{10-5} samples were 180 and 207 m^2/g. Due to their large SSAs and tiny particle sizes, the reactivity of the samples with respect to metal ion adsorption revealed pseudo adsorption capacities of 3425 mmol Pb^{2+}/kg and 1789 mmol Zn^{2+}/kg. After 120 min at room temperature, 97% of the MB was adsorbed, and approximately 68% was oxidized (Figure 2). The adsorbed amount and the level of oxidation increased with increasing temperature and decreased with increasing pH.

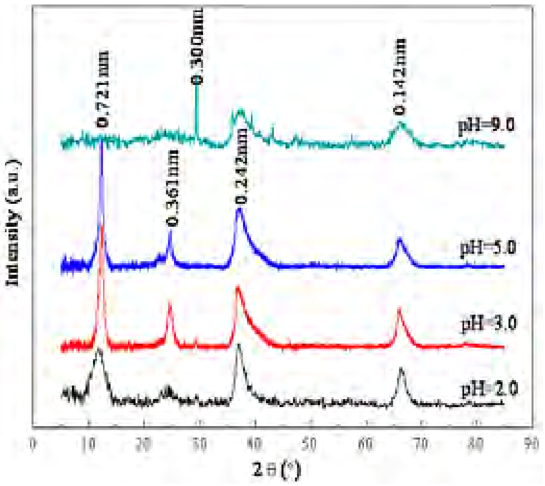

Figure 1 XRD patterns of samples synthesized at a $KMnO_4$/AA of 10 and different pH values

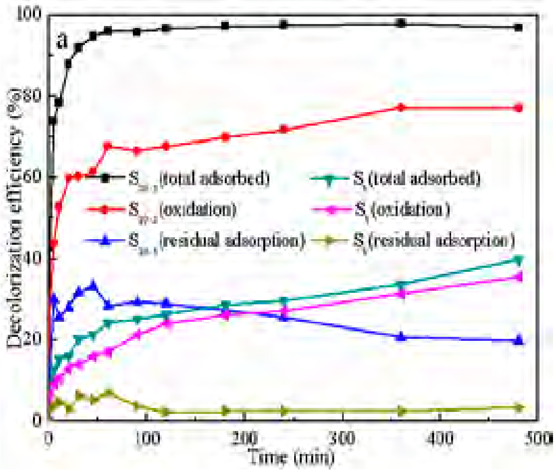

Figure 2 MB decolorization efficiency of the tested samples at 25 °C over different reaction times

Effect of Soil Colloidal Properties on Surface Runoff from Tottori Masa Soil

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We investigated the relationship between interfacial chemical properties of Tottori Masa soil and the surface runoff from the soil induced by raindrops generated with a compact rainfall simulator.

The zeta potential of the soil colloidal particles demonstrated that the soil has pH-dependent negative charge; the absolute values of the zeta potential of the soil increase with increasing pH. The soil particles flocculated when the magnitude of zeta potential was low and the salt concentration and the valence of counter ions were high. These results suggest that flocculation-dispersion behavior of the soil follows the DLVO theory [1].

Figures 1 and 2 show the effects of pH and counter ion type on the surface runoff from Tottori Masa soil. The surface runoff increased with increasing pH, suggesting that the runoff was enhanced under dispersed condition (Fig.1). This finding is in good agreement with the result of zeta potential. We consider that, at dispersed state, detached particles produce surface crust with low hydraulic conductivity. While both 1 mM $CaCl_2$ and 10 mM NaCl are in the rapid coagulation regime where the electric repulsion is negligible, the runoff induced by 1 mM $CaCl_2$ rainfall was less than that by 10 mM NaCl. This behavior cannot be explained by the DLVO theory. We consider that calcium ions provide an additional particle-particle binding force [2] and thus reduce the surface runoff by inhibiting the formation of soil crust.

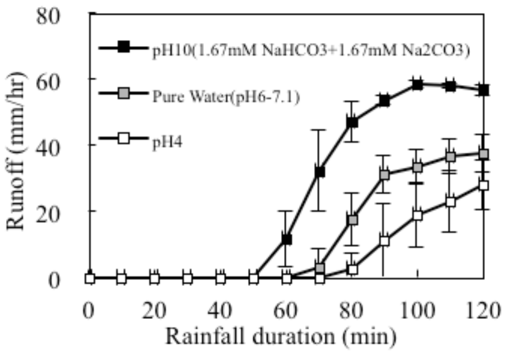

Figure 1 Effect of pH on runoff from Tottori masa soil. Rainfall intensity was 71.5±6 mm/h (vertical bars denote a standard derivation).

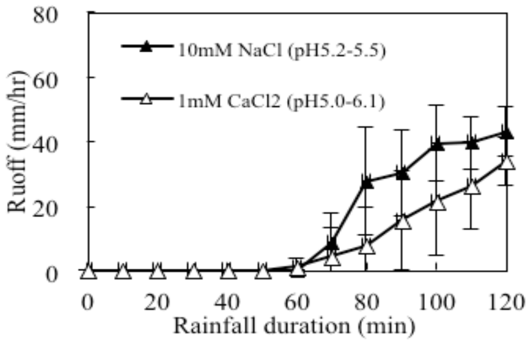

Figure 2 Effect of electrolyte on runoff from Tottori masa soil. Rainfall intensity was 71.5±6 mm/h(vertical bars denote a standard derivation).

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The Mechanism of degradation on 4-Chlorophenol by Pulse Radiolysis

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The aim of the reactions of ·OH radicals generated by radiolysis in N_2O-purged aqueous solutions with 4-chlorophenol(4-CP) have been investigated, especially focusing on the addition to the aromatic rings and the direct electron transfer of ·OH radicals. Using the pulse radiolysis technique, different absorption spectral features of the short-lived transients which are produced by reaction with ·OH radicals at different pHs and the their corresponding rate constants have been determined. The results showed that ·OH preferentially added to the aromatic ring forming 4-chlorodihydroxycyclohexadienyl radical, which had a strong adsorption at 310nm, and it followedby the second-order reaction which the rate constant was measured in acid and neural condition, as $2.86\times10^9 L^3 mol^{-1} s^{-1}$ and $4.1\times10^9 L^3 mol^{-1} s^{-1}$, respectively. In addition, in order to give good selective oxidation to get chlorinated phenoxyl radical, azideradical($\cdot N_3$) and sulfate radical($SO_4^{-}\cdot$) have been shown. The results suggested that the formation of 4-chlorophenoxyl radical was attributed to direct electron transfer and dehydration of 4-chlorodihydroxycyclohexadienyl radical. And the adsorption spectrums of this chlorinated phenoxyl radical should be at 350nm and 400nm. In neutral aqueous solution, the 4-chlorodihydroxycyclohexadienyl radical was the dominant short-lived intermediate formed during the period of radiolysis of 4-chlorophenol.

Keywords: Mechanism of degradation; 4-Chlorophenol; Pulse Radiolysis; Rate Constants

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Transport and retention of multi-walled carbon nanotubes in different porous media

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The applications of multi-walled carbon nanotubes (MWCNT) will inevitably lead to their release into environment but little is known about the fate and behavior of MWCNT when exposed to environment. This study deals with the transport and retention of MWCNT in different porous media (quartz sands, silty loam and loamy sand) at different input MWCNT concentrations and low flow rates. MWCNT concentrations in the effluent and in the porous media were determined for breakthrough curves and retention profiles. To more accurately understand the fate of MWCNTs, the breakthrough and deposition data collected were simulated by using HYDRUS-1D. In quartz sands, results demonstrate that normalized MWCNT transport increased with higher input concentrations and in coarser textured sand. The retention profiles showed that the majority of MWCNT retention occurred near the surface of the porous medium, especially for lower input concentrations and smaller sand sizes. In undisturbed soils, results revealed almost complete retention of functionalized MWCNT. More than 86% of MWCNT were recovered in the soil profile at conditions close to saturation. At lower water-saturation, MWCNT retention in the upper soil layers was enhanced. The co-transport of the pesticide Chlordecone in different porous media will also be discussed in this paper.

Direct Electrochemistry of Horseradish Peroxidase based on Carbonized Chicken Eggshell Membranes Materials

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The eggshell membrane is a reliable and sustainable resource for clean energy storage as over 1000 billion eggs are consumed per year globally. Nanoscale carbon electrode materials are synthesized by carbonizing a daily available biowaste in the form of chicken eggshell membranes (CESM). The structure of modified electrode was characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results showed it was a three-dimensional carbon film composed of interwoven connected carbon fibers (Fig. 1). Two obvious redox peaks and an excellent current response (near±1mA) was observed in PBS with a 3-electrode system (Fig. 2). Horseradish Peroxidase (HRP) enzyme was easily immobilized onto the CESM modified glass carbon electrode (GCE). The unique structure and highly electrical conductivity of the CESM material allows establishing very fast direct electron transfer and good biocompatibility between HRP and electrode, making it potentially attractive for the application to biosensor and catalytic degradation.

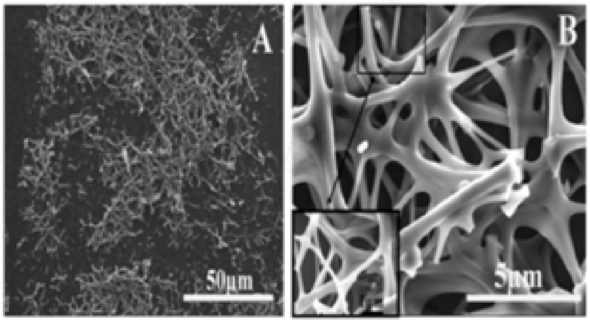

Figure 1 SEM images of CESM-GCE in 50μm(A) and in 5μm (B). The inset is the high-resolution image of the selected area.

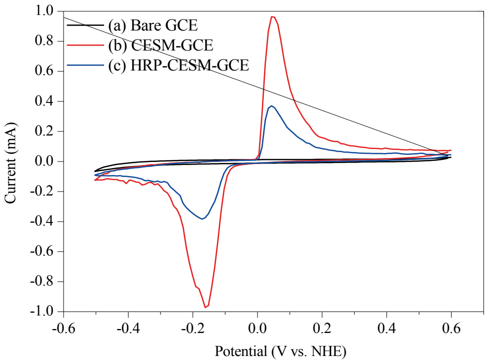

Figure 2 Cyclic voltammograms of pH 7.0 PBS solution, obtained at (a) bare GCE electrode, (b) CESM modified GCE electrode, (c) HRP immobilized CESM-GCE electrode.

Development of Functionalized Graphene Electrode for Water Softening

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The hardness in water represents the contents of divalent ions such as iron, manganese, copper especially, magnesium and calcium. Conventional softening technologies including reverse osmosis (RO) and electrodialysis (ED) for hardness treatment have been developed. However, they still have several disadvantages such as fouling of membrane and high operating cost. Of late, Capacitive Deionization (CDI) is attractive technology for water desalination and softening by very low capacitive current of electrochemical double layer. Among various carbon-based materials used for electrode fabrication, graphene (rGO) has been intensively studied due to its excellent electrical conductivity and high surface area. However, graphene difficultly disperses in water because of its strong Van-der-Vaals force and hydrophobicity, as well as low capacitance causing limitation in making CDI electrode. In this work, we successfully prepared uniformly-dispersed rGO in aqueous solution through control reduction process of graphite oxide and hence enhance ion adsorption ability of in CDI cell system. Additionally, graphene also is composited and activated by MnO_2 in Alkaline condition at high temperature hence, enhance considerable surface area, specific capacitance by MnO_2 presentation as well as improve CDI performance. The effect of parameters to CDI process is investigated in order to optimize the softening efficiency. The voltage of 1.5 V is chose to supply power for this system and maximum ion removals gained can be comparable to other researches.

Keywords: Capacitive Deionization, Graphene, MnO2, Applied voltage, Flow rate.

Enhanced energy generation with capacitive electrodes driven by Exoelectrogen-generated ionic currents

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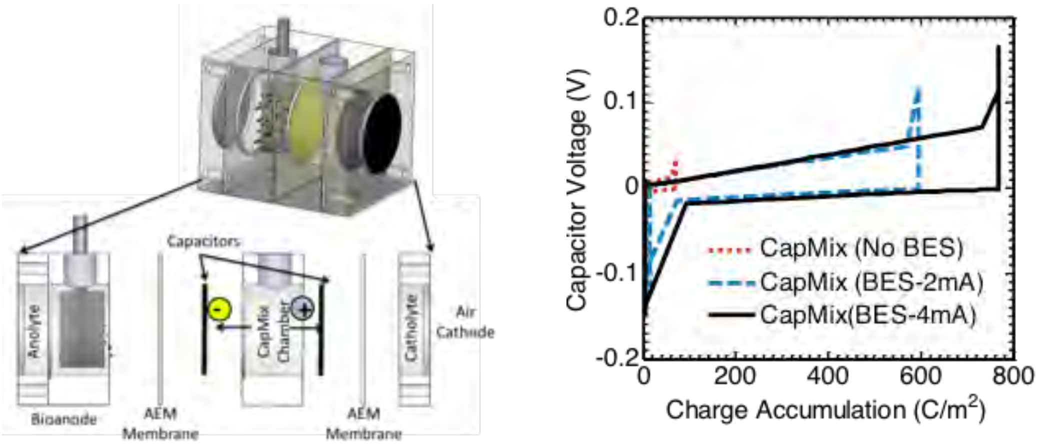
Bioelectrochemical systems (BESs) have the potential to generate electricity through coupling wastewater organics oxidation by bacteria, to a cathodic reaction such as oxygen reduction. Power production from BESs has improved over the last decade, yet still remains on the order of 1-2 W m^{-2} (cathode). The recent synergy between salinity gradient energy technologies (e.g. reverse electrodialysis (RED)) and microbial fuel cells was shown to significantly boost the power from BESs by nearly 5 times [1, 2]. Yet RED currently requires a large number of ion exchange membranes, which results in high cost.

Capacitive mixing (CapMix) is an emerging salinity gradient energy technology which harvests energy through the controlled transfer of ions to and from capacitive electrodes in river and seawater solutions [3, 4]. CapMix has suffered from low power densities, but is still promising because materials cost are low. Experiments were conducted to evaluate the potential synergy between BESs and CapMix (Fig 1a). Results indicated that the presence of the BES electric field improved the charging rate of the capacitive electrodes. This resulted in an increase in the energy harvested from the CapMix process with synthetic river and seawater solutions by 60 times from 0.04±0.003 mJ cycle^{-1} (without BES) to 2.64±0.240 mJ cycle^{-1} (with BES)[5] (Fig 1b). Furthermore, the electric field induced charging mechanism, may have implications for enhancing desalination rates in membrane based capacitive deionization systems.



a)

b)

Figure 1 (a) Capacitive mixing – Bioelectrochemical system schematic and (b) energy extracted from the combined systems as a result of different BES operating conditions.

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Solid-State NMR Studies on Adsorption of Electrolyte Ions in Carbon Materials with well-defined Porosity

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The demand for renewable energy sources and advanced energy storage devices steadily increase in this century of dwindling fossil fuel resources. Among them, electrochemical double-layer capacitors (EDLCs) stand out due to their high power densities and nearly unlimited cycle life [1]. Due to their chemical inertness, high electric conductivity, and large specific surface area, porous carbon materials are used in most EDLCs. Further tuning of their structure and a better understanding of the relationship between their properties and the EDLC performance is highly desired. Recently, Chmiola *et al.* found that there is a capacitance increase when the pore size of the carbon materials becomes lower than the critical solvent shell size and the formation of a double-layer would not be possible from the theoretical point of view [2]. These findings forced the development of novel microporous carbon materials for the use in EDLCs as well as the use of new techniques for the characterization of the carbon-electrolyte interaction. Next to small-angle neutron scattering and theoretical simulations especially nuclear magnetic resonance spectroscopy (NMR) was found to be a useful method for the investigation of the ion adsorption in microporous carbons [3-4].

In the present contribution a series of porous carbon with well-defined pore sizes ranging from 0.6 nm to 4.5 nm is used for solid-state NMR investigations on the adsorption of Tetraethylammonium-tetrafluoroborate ($TEABF_4$) ions (1M solution in acetonitrile). Our investigations focus on ordered mesoporous carbide-derived carbons (OM-CDCs), mesoporous CMK-3, and microporous CDCs. Materials are loaded with the electrolyte solution or the pure solvent for comparison. Magic angle spinning (MAS) ^{1}H, ^{11}B, and ^{13}C NMR measurements show that the chemical shift of NMR active nuclei located at molecules adsorbed in porous carbon materials of comparable degree of sp^2 hybridization is strongly correlated with the pore size [5]. However, the characteristic diamagnetic shift is clearly influenced by the hybridization state of the carbon atoms. In carbon materials with sufficiently large pores, electrolyte molecules tend to reside closer to the pore walls than the solvent molecules (AN) which are to some extent “screened” from the influence of the pore walls by the electrolyte. Removal of the solvent by evacuation results in a removal of the solvent shell and brings the electrolyte molecules into closer contact with the pore wall. If adsorbed in pores <1 nm diameter, solvent removal does not result in a further increase of the diamagnetic shift. This supports the idea that the electrolyte molecules do not exhibit an intact solvent shell in such small pores.

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Temperature and size effects on the desalination of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigate the effect, which either varying the temperature or the pore and engine sizes have on the properties of blue engine and desalination cycles. Desalination cycles were found to be most effective when a huge bath of cold water is used. There is a ~10% decrease in required energy when changing from equatorial to arctic sea water and another ~10% decrease when changing the volume of the desalination bath from the volume of the engine to a 10x larger one.

Furthermore, we studied the effect of using water at different temperatures and electrodes build from pores of different sizes within one cycle. Saline water reservoirs at different temperatures can be obtained by e.g. pumping sea water from depths to the surface or by using cooling water from industrial facilities in an intelligent way. Desalination becomes increasingly cheap when performing the charging step in sea water of lower temperature than the discharging step. Interestingly, the characteristics of the engine (pore size, pore volume, bath volume) can be tailored such that the required energy vanishes already for small temperature differences.

These positive temperature and size effects on the efficiency are not at all exclusive to desalination cycles; similar effects are also observed in blue energy cycles. We find that blue energy harvesting can be enhanced when fresh water is used which has a higher temperature than the sea water. For large temperature differences of the order of 50 degrees this boosts the work per cycle by a factor of two, compared to existing techniques (see figure).

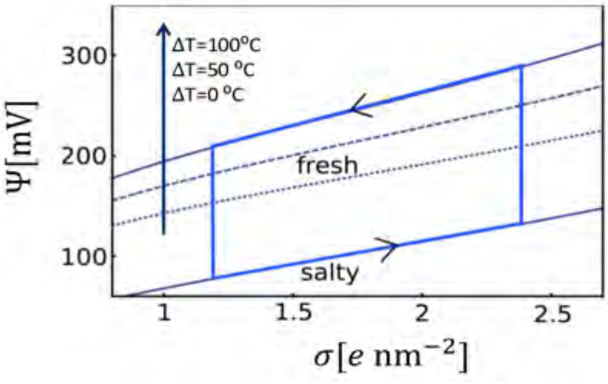

Figure Blue energy cycle in the potential – charge representation. Stroked lines represent the upper part of the cycle, connected to fresh water reservoirs of different temperature.

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Preparation of Chestnut-like Carbon Electrodes for Capacitive Deionization

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Recently, the reliable supply of clean fresh water is becoming increasingly difficult as global and regional development accelerates, and this has become a bottleneck issue for the sustainable development of many countries. Chestnut-like carbon were prepared PCNFs grown on activated carbons using the catalytic gasification with Fe - Ni catalysts in air. Catalytic gasification of activated carbon was carried out at 400 for 1 h at each temperature. The PCNFs grown on activated carbon at 600 °C using activated carbon gasified with a 0.1% Ni-Fe catalyst at 450 °C. The surface area of Chestnut-like carbons were 2401 m2/g. Additional specific capacitances of Chestnut-like carbon are significantly higher than those of other activated carbons. Chestnut-like carbon electrodes show approximately 44% retention of the specific capacitance, which is higher than that of the virginity activated carbon. Thus, Chestnut-like carbon electrode can be predicted to yield better performance in the capacitive deionization (CDI) process.

Multidisciplinary modelling of CDI using optimisation tools: implications for agricultural applications

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Capacitive deionization is a viable method of water treatment in an increasing number of small scale and niche applications but is less cost effective at higher volume applications above the megalitre per day range. As the per-gram cost of adsorbent materials decreases with advancements in manufacturing and design, CDI could become the answer to significant environmental challenges of larger scale. The work presented here addresses the issue of scale up with particular attention given to the accuracy of process costing and optimisation. Models of the physical aspects of CDI developed by Biesheuvel et al (2009[1], 2011[2]) are used as the basis of the modelling undertaken here with the optimisation tool AspenTech used to obtain a more accurate estimate of process level performance as a function of key design and process variables. In particular, consideration is given to possible CDI configurations within a conceptualised large scale process and the Aspen modelling package used to examine impact of process variables on cost effectiveness. The implementation of CDI in the simulation environment is undertaken via a custom module utilising a discretised form of the available physical models of the CDI process. The optimisation package developed enables rapid identification of suitable applications in situations where reverse osmosis has shown to be non-viable. In this analysis we focus on treatment of brackish water for use in agriculture/horticulture with particular attention given to the impacts of water demand and brackish water quality on optimal choice of process parameters and viability of the proposed technology. Further development of this modelling framework could provide the impetus to attract the resources needed to further accelerate the cost reduction process.

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Water Denitrification using Energy-Efficient Capacitive Deionization Technology

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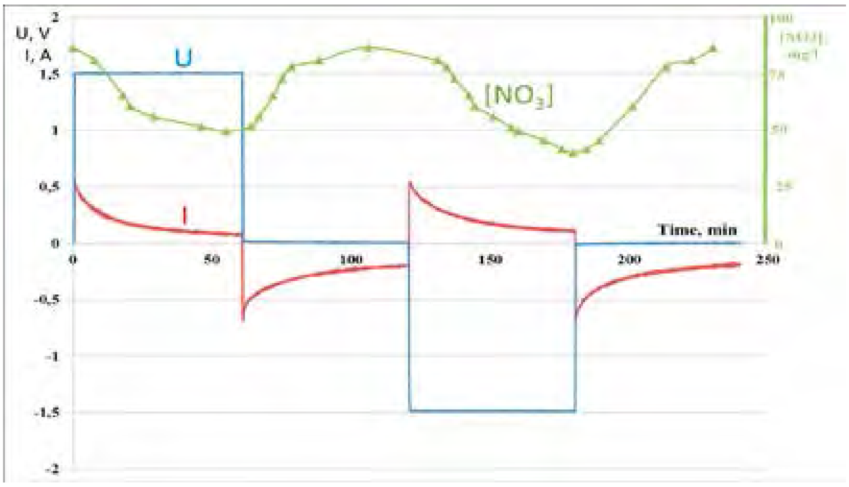
Recent water quality monitoring has shown the ingress of nitrates into the groundwater. The over-application of fertilizers results in the increased nitrate level and the exceeding maximum permissible concentration (MPC) for nitrates in many areas around the world that is a big risk for human health. Therefore, the importance of creation and development of water denitrification technologies grows year after year.

The results of the investigation on nitrate sorption in the CDI units are presented in the paper. The electrodes for the CDI units were manufactured from carbon material SAUT-1C which was modified by titanium. Deposition of titanium coating was made using the Arc-PVD method. Weighted samples of pure chemicals as well as distilled water were used for preparation of standard aqueous solution. The solution was circulated in a circle. The total volume of the solution was 4,7 L, and the circulation flow rate of the solution was 1 L/min. The ion concentration was measured using the potentiometric method, and the total salt content was controlled using the conductometric method. The measurements were made in a buffer volume. The programmable low-voltage power supply unit CDS1-5M10 was used to supply the electrochemical module with power. The power supply unit includes five separate modules with each having the operating voltage range of -1,5 V ÷ +1,5 V as well as the operating current range of 0-10 A.

The typical current and voltage oscillograms of the CDI units within the charging-discharging cycles as well as the variation in nitrate concentration level of the treated solution are shown in the figure. The decrease of the nitrate concentration by several times (2-5) to the level below the MPC for nitrates (45 mg/l) was demonstrated. The adsorption of sodium, potassium, calcium ions and chlorides was also studied. It was shown that the ion adsorption is inversely proportional to the ion valency in aqueous solution. Thus, for the same total transferred charge the number of calcium ions being adsorbed on the electrode surface is twice less than the number of monovalent sodium ions that corresponds to the ion valency. It was also shown that the specific adsorption ability of the carbon material SAUT-1S modified by titanium for sodium chloride solution (5000 ppm) is 15,3 mg per 1 g of carbon material.

Therefore, it was shown that the CDI technology can be applied for water denitrification as an energy-efficient method.



Fabrication of composite capacitive deionization electrodes using biochar materials and conductive membranes

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Capacitive deionization (CDI) is considered as a promising and sustainable technique for energy storage and brackish water desalination. However, the material selection and fabrication of low cost electrodes is one of the main limiting factors for large-scale commercial applicaiton of CDI technology. In this study, composites of low-cost and renewable biochar, produced from woody biomass and a conductive polymer, PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) are evaluated as CDI electrodes. PEDOT:PSS is a promising candidate to improve the intra-particle conductivity and ion adsorption capacity of the electrode system due to its high conductivity, processibility, effective binding material, and environmental stability, and low cost. The compatibility of PEDOT:PSS with mesoporous carbon shows applicable potential to apply the PEDOT:PSS/tailed-carbon system in CDI chambers. The salt adsorption/desorption efficiency is measured in constant potential and cyclic voltammetry experiment and the electrochemical property of the electrode is studied by using impedance spectroscopy. The performance of fabricated electrodes will be compared to biochar capacitive electrodes fabricated with a conventional binding agent (i.e. PVDF).

Keywords: Capacitive deionization, Biochar supercapacitor, Conductive polymers, CDI flow design.

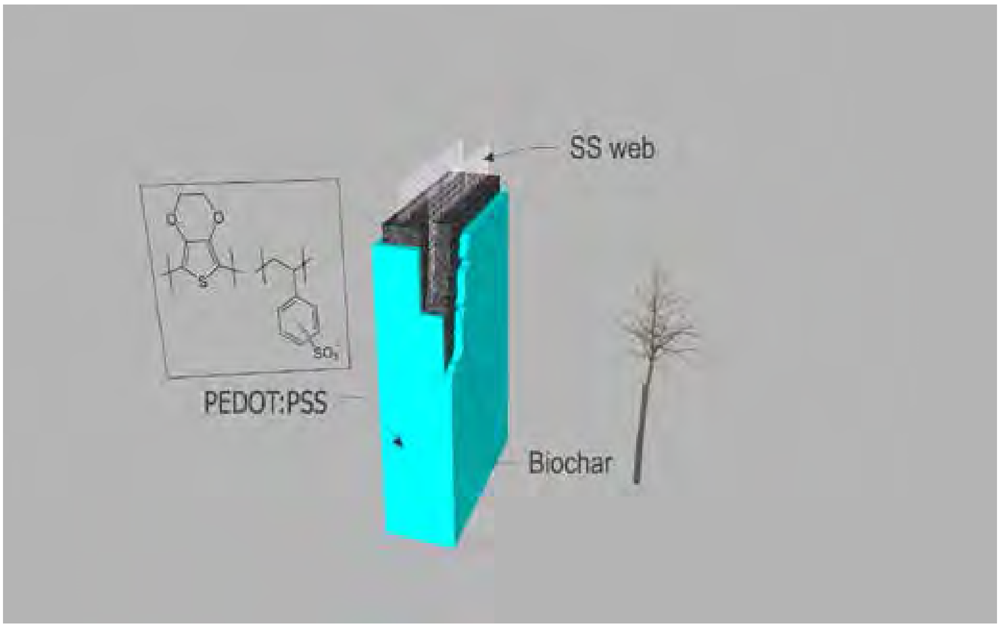

Figure CDI electrode constructed with biochar, stainless steel web, and PEDOT:PSS conductive polymer.

Electrokinetic remediation of fine clay soils contaminated by Hydrophobic organic pollutants

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Active accumulation of hydrophobic organic compounds in the environment sets the task of the development of effective methods directed to their removal from water, sludge and soils. The most problematic objects for decontamination are dispersions, which contain fine clay components. First of all, due to peculiar surface and volume properties and large specific surface area of this type of dispersions, they are the most inclined to retain pollution. Secondly, due to the high values of hydrodynamic and aerodynamic resistances, the choice of effective decontamination method is extremely limited.

Electrokinetic treatment is the method for which the fine clay soil specific properties ensure its effectiveness in removing of uncharged organic compounds. For the effective management of the process it is necessary to provide a stable electroosmotic flow and to reach water-solubility of hydrophobic contaminants.

The rate of electroosmotic transport depends on the zeta potential of soil particles, which in turn depends on the pH of a pore solution. Thus, the important aspect of soil decontamination is regulation of pH. Electrohydrodynamic method of regulation of pH and intensification of electroosmotic permeability for enhancing the efficiency of the removal of hydrophobic organic compounds is proposed and theoretically and experimentally substantiated.

Another aspect is the correct choice of surfactants, which provide desorption and movement of hydrophobic contaminants into the pore solution. Cationic surfactants can not be used since clay soils have a negative electrokinetic potential, which decreases upon introduction of positively charged surfactants leading to a diminution of the electroosmotic velocity. Introduction of anionic surfactants increases the electrokinetic potential of soil particles accelerating electroosmosis, but in the same time these surfactants can charge the organic compounds leading to their electromigation in the direction opposite to electroosmotic flow, thereby also slowing down the rate of soil decontamination. Finally, nonionic surfactants do not charge the organic pollutants and therefore do not affect the velocity of electroosmosis. Thus, they are the most promising in soil remediation.

Studies of the effect of the type of surfactants on soil remediation efficiency were carried out on a model system, which is kaolinite contaminated by ortho-chlorotoluene (4.5 mg/g of kaolinite) using non-ionic surfactants (Triton X-100, Tergitol 5-S-7, Neonol AF-9-12) and anionogenic surfactant (sodium dodecyl sulfate).

The obtained experimental data demonstrated that the presence of anionic surfactant results in a significant increase of the velocity of electroosmosis in comparison with the velocity at the use of nonionic surfactants. For example, at the electrokinetic remediation with the use of sodium dodecyl sulfate 160 ml of electroosmotic liquid (10 volumes of pore solution) passed through the soil during 20 hours, while the introduction of a Triton X-100 increased the treatment time to 36 hours. However, as expected, anionogenic surfactant significantly reduced decontamination efficiency - 70.7% of residual ortho-chlorotoluene compared to 26.0% in the case of non-ionic one that is caused by appearance of their own electromigration mobility

The velocities of electroosmosis for different nonionic surfactants are almost the same, but the degree of pollutant removal is much different. Tergitol 5-S-7 provided decontamination almost at the same level as it was obtained at presence of Triton X-100 (27.7% of the residual ortho-chlorotoluene). The best results were obtained for Neonol AF-9-12 (at the passage of 160 ml of electroosmotic liquid the residual ortho-chlorotoluene decreased to 5.7%). The increase of the treatment time allows to decrease the residual ortho-chlorotoluene to the rather small values, however this is accompanied with increase of power consumption.

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