IAP2018
INTERFACES AGAINST POLLUTION

LA GRANDE MOTTE, FRANCE
10-13 JUNE 2018

ABSTRACT
BOOK

CHAIRS

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University of Montpellier, France

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The event is organised by the members of the **Charles Gerhardt Institute of Montpellier** and the **Marcoule Institute for Separation Chemistry**

BOOK OF ABSTRACTS

LA GRANDE MOTTE
10-13 June 2018

The 10th International Conference on Interfaces Against Pollution

On behalf of the Organising Committee, we are pleased to welcome you all to the 10th international conference on Interfaces Against Pollution (IAP), which will celebrate the 20th anniversary of the IAP conference series. Subsequent IAP conferences were held in Wageningen (The Netherlands, 1997), Miskolc (Hungary, 2002), Jülich (Germany, 2004), Granada (Spain, 2006), Kyoto (Japan, 2008), Beijing (China, 2010), Nancy (France, 2012), Leeuwarden (Netherlands, 2014), and most recently in Lleida (Spain, 2016).

The rapidly growing global population together with the general expectation for further improvement of life standards in different parts of the world generate an unending spiral of increasing consumption of food and energy and thus have an enormous impact on the ecosystems. Over the past few decades, there has emerged the overwhelming conviction that the concept of sustainable development needs the integration of environmental concerns and issues into the fields of international politics and economy. Despite a great number of conferences, treaties, directives, action plans, and other instruments proposed at the political level for environment protection, global environmental decline has not been reversed yet. On the other side, the research and technical community continues to provide valuable solutions to environmental protection based mostly on an interdisciplinary approach, as well as scientific support necessary to guide the path of sustainable development in the world. The IAP conference series falls under this heading.

In line with the tradition established during the previous successful IAP conferences, the IAP2018 edition has the ambition to bring together international researchers who conduct impactful research that transcends disciplinary boundaries in addressing the key role played by (bio)interfaces and (bio)colloids in complex environmental processes and media. We sincerely hope that fundamental and solution-oriented research contributions presented during the three days of the conference will represent a notable step towards understanding and control of interfacial and colloidal processes operative in model, engineered, or natural systems, all of which are necessary to achieve a mechanistic evaluation of the action of soil, sediment, and aquatic environments or to develop environmental remediation technologies.

By choosing the resort town of La Grande Motte within the Mediterranean region as the conference venue, away from the bustle of the city, our aim has been to provide a relaxed atmosphere to promote more creative and productive thinking and exchange of ideas. We shall be happy to make you discover the Camargue and Petite Camargue, one of Europe's major wetlands, as well as the Pont du Gard, one of the world's best-preserved examples of Roman ingenuity, recognized as world heritage by UNESCO since 1985.

Jerzy ZAJAC (Chair)
Jean-François DUFRÊCHE (Co-Chair)

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PRETEXO

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Nathalie Tufenkji, *Canada*

Scientific and Social Programme

Sunday 10 June 2018

18:00 – 20:00 Welcome cocktail and Registration
(in the entrance hall of the Palais des Congrès of La Grande Motte)

Monday 11 June 2018

8:00 – 18:00 Registration
(in the entrance hall of the Palais des Congrès of La Grande Motte)

8:30 – 8:45	**Welcome and Opening Remarks** *(in the Small Auditorium of the Palais des Congrès)*	
8:45 – 9:30	**Plenary Session N° 1 –** *Small Auditorium*– Chair: J. Zajac **PL1:** Irene M. C. Lo, *Removal of PPCPs in Wastewater using Recyclable Visible light driven Superparamagnetic Bismuth Oxyhalide*	
9:30 – 10:00	*Coffee break*	
10:00 – 12:30	**Session N°1 –** *Small Auditorium* Chairs: J.F.L. Duval + J. Puy	**Session N°2** - *Room "Camargue"* Chairs: A.V. Delgado + P. Hesemann
10:00 – 10:30	**KN1:** J. Pena, *Redox reactivity of manganese oxide nanoparticles: Sustaining water and soil resources*	**KN2:** C. Grison, *Ecocatalysis: an unsual combination of Ecology and Bio-inspired Chemistry for tomorrow's chemistry*
10:30 – 10:50	**OM1:** S. Benkaddour, *Influence of vacancy sites and Mn(III) atoms on MnOx photoreduction*	**OM7:** A. Tiraferri, *Tuning the injection and immobilization of reactive nanoparticles in the aquifer for an effective site remediation*
10:50 – 11:10	**OM2:** G. Farinelli, *Oxidation mechanism and efficacy of iron(II) complexes to be applied in the heterogeneous degradation of organic contaminants*	**OM8:** T. Serra, *Daphnia magna filtration efficiency and mobility in sheared flows*

11:10 – 11:30	**OM3:** E. Subdiaga, *Electron Exchange Capacities of Humic Acid Sorbed to Redox Active Clays*	**OM9:** M. Rivallin, *TiOx reactive electrochemical membranes for the removal of organic pollutants from water: process and material optimization*
11:30 – 11:50	**OM4:** J. Hou, *Morphology-dependent enhancement of arsenite oxidation to arsenate on birnessite-type manganese oxide*	**OM10:** I. Lakehal, *Fast elaboration of chitosan porous beads and selective adsorption of heavy metals by complexation*
11:50 – 12:10	**OM5:** G. Carrasco, *Zinc and Zinc-complexing ligands from rivers and anthropogenic activity in coastal South East Asia and around Singapore*	**OM11:** T.-H. Chou, *Treatments to Degrade Polybrominated Diphenyl Ethers in Water and Their Feasibility to Contaminated Soil*
12:10 – 12:30	**OM6:** D. Hausladen, *Stability and reactivity of biogenic Mn oxides in the presence of natural organic matter*	**OM12:** P. Behra, *Boron removal by selective and anionic resins from batch and column experiments*
12:30 – 14:00	*Lunch*	
14:00 – 16:10	**Session N°3** – *Small Auditorium* Chairs: T. Saito + L. Koopal	**Session N°4** – *Room "Camargue"* Chairs: M. Avena + R.M. Town
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14:30 – 14:50	**OM13:** Y. Adachi, *Effects of Mixing Intensity on the Flocculation Kinetics of Colloidal Particles*	**OM18:** A. Voegelin, *Arsenate uptake by fresh and aged Fe oxidation products*
14:50 – 15:10	**OM14:** O. Diat, *Ion and particle foam flotation for aqueous phase remediation*	**OM19:** L. Castro, *Heavy metals sorption from industrial effluents using biogenic iron compounds*
15:10 – 15:30	**OM15:** A S. Le Crom, *Simulation of unsaturated clay pores at the microscopic scale*	**OM20:** E. Rotureau, *Structural effects on thermodynamics of metal binding with responsive core-shell nanoparticles*
15:30 – 15:50	**OM16:** M. Špadina, *Charge properties of TiO_2 nanotubes in $NaNO_3$ aqueous solution*	**OM21:** J. Antelo, *Mechanistic study of the ion binding behaviour of iron oxides and organo-mineral composites*
15:50 – 16:10	**OM17:** J. Saab, *Vapor pressure and aqueous solubility measurements of phthalates and phenols contained in recycled food packages*	**OM22:** J. Groenenberg, *Solid-solution partitioning of Rare Earth Elements in mine-tailings and soils in China: experimental results and multi-surface modelling*
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16:30 – 18:10	**Session N°5** – *Small Auditorium* Chairs: J. Galceran + M. Jardat	**Session N°6** – *Room "Camargue"* Chairs: A. Tiraferri + P. Behra
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Tuesday 12 June 2018

8:00 – 15:00 Registration

(in the entrance hall of the Palais des Congrès of La Grande Motte)

8:45 – 9:30	**Plenary Session N° 2** – *Small Auditorium* – Chair: B. Prélot **PL2:** T. B. Hofstetter, *New Challenges for the Stable Isotope Analysis of Organic Contaminant Biodegradation*	
9:30 – 10:00	*Coffee break*	
10:00 – 12:30	**Session N°7** – *Small Auditorium* Chairs: Y. Mishael + Irene M. C. Lo	**Session N°8** - *Room "Camargue"* Chairs: Y. Shih + V. Ogurtsov
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10:30 – 10:50	**OT1:** Q. Albert, *Screening of fungal isolates collected from soils in the bioremediation of Trace Metals (Cd, Cu, and Pb)*	**OT7:** R. Le Parc, *Investigation of retention mechanisms of dye by lamellar materials through vibrational spectroscopy*

10:50 – 11:10	**OT2:** N. Goykhman, *Transport of Oxaliplatin and Carboplatin in Natural Soil-Water Environments*	**OT8:** M. Avena, *Surface species of phosphate on goethite. Distribution as a function of pH and surface coverage*
11:10 – 11:30	**OT3:** N. Pous, *Assessment of zooplankton for domestic wastewater treatment*	**OT9:** A. Beaussart, *Nanoparticle (NP) interactions with (bio)surfaces probed by single-NP force spectroscopy*
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11:50 – 12:10	**OT5:** C. Catrouillet, *As removal in Mn-contain groundwater matrices*	**OT11:** A. Radian, *Quinone Interactions with Iron Bearing Clays and Oxides*
12:10 – 12:30	**OT6:** M. Sander, *Biodegradation of aliphatic polyesters in soils: using stable carbon isotope labeling to track polyester-derived carbon*	**OT12:** K. Bohinc, *Interactions between charged macroions mediated by nanoparticles with spatially distributed charges*
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15:30 – 23:40	*Tourist tour + Gala Dinner (Pont du Gard)*	

Wednesday 13 June 2018

8:00 – 16:00 Registration

(in the entrance hall of the Palais des Congrès of La Grande Motte)

8:45 – 9:30	**Plenary Session N°3 –** *Small Auditorium* – Chair: J.F. Dufrêche **PL3:** J. Gardea-Torresdey, *From Searching for Friendly Mining Technologies to Studies on the Chemical Fate of Nanoparticles in Terrestrial Plants: How Gold Mining Changed My Life*	
9:30 – 10:00	*Coffee break*	
10:00 – 12:30	**Session N°9** – *Small Auditorium* Chairs: Y. Adachi + M. Sander	**Session N°10** - *Room "Camargue"* Chairs: J. Gardea-Torresdey + T. Hiemstra
10:00 – 10:30	**KN7:** J. Galceran, *AGNES: a tool for studying the thermodynamic and kinetic behaviour of nanoparticles*	**KN8:** R.M. Town, *The lability of nanoparticulate metal complexes at a macroscopic interface: the reaction layer concept revisited*
10:30 – 10:50	**OW1:** P. Trens, *Tuning the hydrophilic-hydrophobic balance of*	**OW7:** M. Aeppli, *Coupled analyses of changes in iron oxide mineralogy and*

	Prussian Blue analogues for the removal of toxic gases in humid atmosphere	*reducibility during ferrous iron catalysed transformation of ferrihydrite to goethite and magnetite*
10:50 – 11:10	**OW2:** M. Jardat, *Coarse-grained model of sodium polyacrylate in montmorillonite*	**OW8:** W. Tan, *Contribution of Soil Active Components to the Control of Heavy Metal Speciation and Modeling*
11:10 – 11:30	**OW3:** L. Duclaux, *Fenton treatment using iron nanoparticles supported on activated carbon from banana spike: Rhodamine B removal and treatment of dyeing wastewater*	**OW9:** J. Korchowiec, *Modeling lung surfactant interactions with benzo[a]pyrene*
11:30 – 11:50	**OW4:** S. Wick, *Importance of illite for Tl uptake in soils*	**OW10:** Ch. Ligoure, *Bursting mechanism of emulsion based liquid sheets: anti-drift application for agricultural sprays*
11:50 – 12:10	**OW5:** Y. Mishael, *Polycyclodextrin-Clay Composites: Regenerable Dual-Site Sorbents for Bisphenol A Removal from Treated Wastewater*	**OW11:** E. Belut, *Aerosol scavenging by droplets: impact of rear capture for low inertia aerosol and moderate to transitional Reynolds number*
12:10 – 12:30	**OW6:** R. Marsac, *Influence of magnetite stoichiometry on the binding of emerging organic contaminants*	**OW12:** L. Ramos, *Interfacial behaviour of plant proteins*
12:30 – 14:00	*Lunch*	
14:00 – 15:50	**Session N°11** – *Small Auditorium* Chairs: W. Tan + J. Pena	**Session N°12** - *Room "Camargue"* Chairs: T. B. Hofstetter + G. Lefèvre
14:00 – 14:30	**KN9:** T. Saito, *Cadmium binding and formation of nano-sized particles with humic acid extracted from deep sedimentary groundwater*	**KN10:** V. Ogurtsov, *Electrochemical sensing system for environmental applications*
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15:10 – 15:30	**OW15:** A. Otero-Fariña, *NICA-Donnan Modelling of Rare Earth Element binding to humic substances*	**OW19:** J.P. Pinheiro, *Development of a Flux DMT with integrated Adsorptive Stripping Voltammetry for free metal ions detection in solution*

15:30 – 15:50	**OW16:** P. Picot, *Methyl-imogolite: a new hybrid nanotube for water remediation*	**OW20:** M. Gledhill, *Release and fate of explosive compounds (TNT, RDX, HMX) from discarded munitions in the Baltic Sea*
16:00	**Closing Ceremony** *(in the Small Auditorium of the Palais des Congrès)*	

ORAL PRESENTATIONS

PL1

Removal of PPCPS in wastewater using recyclable visible-light-driven superparamagnetic bismuth oxyhalide

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Pharmaceuticals and personal care products (PPCP) are an emerging class of aqueous pollutants with associated risks to human and aquatic life. Photocatalysis is an environmentally friendly treatment technology, but the traditional photocatalysts are only activated by UV light (only ~4% of the solar spectrum) and their separation from water/wastewater is difficult due to their nano-size. In this study, a visible-light-driven superparamagnetic photocatalyst ($BiOX/Fe_3O_4@SiO_2$ where X denotes halogen) was synthesized by embedding silicon dioxide coated magnetite ($Fe_3O_4@SiO_2$) nanoparticles within the 3D hierarchical BiOX microspheres through a solvothermal process. Due to the magnetic property, the superparamagnetic photocatalyst can be recovered and reused which in turn can save the treatment cost. A suite of material characterization techniques, including TEM, SEM, EDS, BET/BJH, XRD, XPS, UV-vis DRS, and VSM, were employed to determine the physical, chemical, optical, and magnetic properties of $BiOX/Fe_3O_4@SiO_2$. The bandgap determined through UV-vis DRS indicated its capability to perform under visible-light. The magnetic properties measured by VSM showed that it was of a superparamagnetic nature with sufficiently high saturation magnetization. The $BiOX/Fe_3O_4@SiO_2$ achieved complete PPCP degradation within an hour of visible-light-irradiation. The mechanistic investigation — comprising detection of generated reactive species (e.g., $\bullet OH$, $\bullet O_2^-$, and H_2O_2) and identification of their relative roles — revealed that direct-hole oxidation and $\bullet O_2^-$-mediated reactions are the dominant contributing photocatalytic degradation routes. Reusability of the recycled $BiOX/Fe_3O_4@SiO_2$ was studied over multiple cycles. Based on the findings of batch experiments, the process was scaled up by developing a 5 L prototype photocatalytic reactor integrated with a magnetic separation unit. The results of prototype photocatalytic experiments were comparable to that of batch experiments, and a magnetic separation efficiency of ~99% was achievable in 5 min using the magnetic separation unit. Overall, the results of this study indicate the promising potential of the $BiOX/Fe_3O_4@SiO_2$-based visible-light-driven photocatalytic process integrated with magnetic separation in practical applications.

Acknowledgements- The author gratefully acknowledges the financial support from Innovation and Technology Commission under the Innovation and Technology Fund (ITS/024/16 account) for this research.

KN1

Redox reactivity of manganese oxide nanoparticles: Sustaining water and soil resources

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Electron transfer reactions underpin many fundamental processes in environmental systems. The biogeochemistry of major and trace elements, fate of contaminant metals, precipitation and dissolution of redox active minerals and proliferation of microbial communities all emerge from coupled oxidation-reduction (redox) reactions. While typically slow, the kinetics of redox reactions can be enhanced by up to several orders of magnitude by biological activity, short-lived reactive intermediates, mineral surfaces or light. Exploiting recent developments in chemical and spectroscopic approaches, my group has provided new insights on the kinetics and mechanisms of redox processes involving manganese, a key redox-active element in surface environments. This elements exist in multiple oxidation states (II, III, IV), form minerals with a range of structures and reactivity, and has critical biological functions.

In this talk I will focus on the molecular-scale mechanisms of manganese oxide reduction when coupled to the oxidation of the redox-active metals and organic species water. Previous spectroscopic studies have relied on the use of batch experiments to study contaminant oxidation by birnessite. However, such studies can obscure the reaction mechanism. Recently, we investigated the redox reactivity of MnO_x through time-resolved measurements of surface speciation (1, 2). Kinetic studies of Co oxidation by δ-MnO_2 coupled to quick X-ray absorption spectroscopy provided the data necessary to address three key questions regarding the ability of MnO_2 to oxidize contaminant species: What is the reactivity of particle edge sites versus vacancy sites? How do the amount and crystallographic location of Mn(III) centers influence redox reactivity? How does the reactivity of abiotic phases to compare to biogenic phases? Additional kinetic studies using the molecule 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid (ABTS) as a probe redox provide a framework to assess structure-reactivity relationships for Mn oxides phases. This research elucidates how manganese oxides drive critical biogeochemical processes and informs the potential to implement these Earth materials in strategies for contaminant transformation and sustainable technology development.

References

[1] Simanova AA, Pena. Time-Resolved Investigation of Cobalt Oxidation by Mn(III)-Rich δ-MnO_2 Using Quick X-ray Absorption Spectroscopy. *Environmental Science & Technology* 49 : 18, (2015), pp 10867–10876. **DOI:** 10.1021/acs.est.5b01088

[2] Wang Y, Benkaddour S, Marafatto FF, Pena J. Diffusion- and pH-Dependent Reactivity of Layer-Type MnO_2: Reactions at Particle Edges versus Vacancy Sites. *Environmental Science & Technology* 52 : 6, (2018), pp 3476–3485. **DOI:** 10.1021/acs.est.7b05820

OM1

Influence of vacancy sites and Mn(III) atoms on MnO_x photoreduction

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Recent research shows that δ-MnO_2 photoreduction in water occurs through a single electron transfer leading to irreversible Mn(III) formation.[3] This process involves the fomration of a transient layer-Mn(III) atom that leaves the MnO_6 octahedral sheet and creates a vacancy site onto which the photogenerated Mn(III) adsorbs.[3] Photoreduction experiments coupled with XAS measurements confirm the mechanism of Mn(III) photogeneration on a Ni-doped δ-MnO_2 (Ni adsorbed to vacancy sites), where Mn(III) generation leads to Ni release as Ni(aq) and re-adsorption from vacancy sites to MnO_x edge sites.[4] However, these observations were made using a single mineral phase (δ-MnO_2) and one set of reaction conditions. However, we expect that changes in experimental conditions (e.g., mineral phase, light source, background electrolyte, pH) may lead to different rates of Mn(III) photogeneration.

Layer-type MnO_x (birnessite, vernadite) exhibit a range of particle sizes (nm to µm), Mn(III) content and location [0 to 30% present as layer and/or interlayer Mn(III)], and vacancy site density (0 to 20%). While the presence of interlayer Mn(III) is known to lower the sorption reactivity of Mn oxides, its role in the redox cycling of Mn in sunlit aquatic environments has not been well studied and remains unclear.[5] In addition, since increasing vacancy sites content in birnessite structure lowers the mineral band gap,[6] we expect that Mn oxides with higher vacancy content will display enhanced MnO_x (photo)reduction processes. Our study aims to better understand how vacancy content and Mn(III) content/location influence Mn(III)/Mn(II) photo-generation processes.

To investigate the influence of mineral structure on Mn(III)/Mn(II) photogeneration, we selected three manganese oxides with different vacancy and Mn(III) contents (δ-MnO_2, c-disordered birnessite and triclinic birnessite). Aqueous suspensions of these oxides were continuously irradiated over a four-day period using 400 nm LED lights. The suspension was sampled three times per day and was characterized to determine the Mn oxidation state. Aqueous Mn(II) was quantified by ICP-OES analysis on filtered samples. No reductive dissolution of the MnO_x structure was observed for any of the mineral phases. Sodium pyrophosphate (PP) was used to extract solid-phase Mn(III). Mn(III)-PP complexes were quantified spectrophotochemically ($\lambda_{245\ nm}$). Our measurements suggest that vacancy sites presence is critical for Mn(III) photo-generation in birnessite-like structures, however the initial Mn(III) content does not seem to affect the amount of photo-generated Mn(III) over a given period. These finidings strengthen our understanding of the role of manganese oxides in biogeochemical processes and provide insight for the design of materials with specific redox properties.

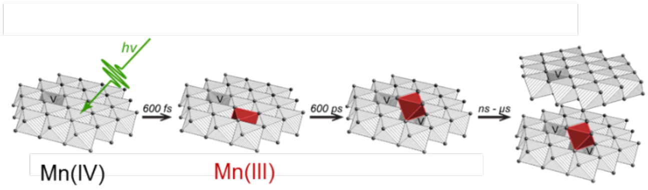

Figure 1: Photo-generation of a Mn(III) atom in the δ-MnO_2 structure. Adapted from reference [4].

References

[1] Bertino DJ, Zepp RG. *Effects of Solar Radiation on Manganese Oxide Reactions with Selected Organic Compounds*. Environmental Science and Technology (1991) 25.

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[4] Marafatto FF, Peña J. *PhD Thesis: The photoreduction of δ-MnO2*. Thèse: Géosciences Environnement - Université de Lausanne (2017).

[5] Peng H, McKendry IG, Ding R, Thenuwara AC, Kang Q, Shumlas SL, Strongin DR, Zdilla MJ, Perdew JP. *Redox properties of birnessite from a defect perspective*. Proceedings of the National Academy of Sciences (2017) 114.

[6] Kwon KD, Refson K, Sposito G. *On the role of Mn(IV) vacancies in the photoreductive dissolution of hexagonal birnessite*. Geochimica & Cosmochimica Acta (2009) 73.

OM2

Oxidation mechanism and efficacy of iron(II) complexes to be applied in the heterogeneous degradation of organic contaminants

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The Fenton process is one of the most effective advanced oxidation processes (AOPs) used in water treatment. However, its implementation is hindered by practical and economic limitations: the process occurs at pH ~ 3 and produces large amounts of sludge to be disposed of. In order to overcome these limitations, we can take inspiration from nature where we find examples of oxidation processes catalyzed by heme or non-heme complexes, such as Cyt P450 or TauD.

The use of iron (II) complexes as catalysts is therefore a very promising variation of the traditional Fenton process. This modification allows the degradation of persistent contaminants at near neutral pH and to cut down sludge production by keeping the iron in solution during the process. However, the interpretation of the reaction mechanism is controversial and this process needs optimization.

In this study, we propose a new approach to understand the reaction mechanism by correlating the structural characteristics of various iron complexes with their reactivity. In addition to offering a contribution to the understanding of the reaction mechanism, this study provides useful data for a systematic optimization of the catalyst chemistry by correlating structural parameters with its reactivity. The final goal is the creation of a heterogeneous phase catalyst allowing contaminant oxidation at the solid/water interface. This presentation focuses on the first part of this study, whereby we evaluate the oxidative mechanism and efficacy of different homogeneous phase catalysts, from which the best ones will be then chosen to construct the solid catalyst.

Eight ligands able to complex iron(II) in a stable fashion were tested. The ligands are: ascorbic acid, citric acid, tartaric acid, malic acid, glutamic acid, EDTA, EDDS, and NTA. These ligands belong to two categories: natural ligands (the first 5 in the list) and synthetic ones (the last 3 in the list). The family of natural ligands tends to form Ligand:Iron 2:1 complexes and the maximum oxidation yield on the target compounds is obtained at slightly acidic pH. The family of synthetic ligands tends to form Ligand:Iron 1:1 complexes and the maximum oxidation yield on the target compounds is obtained at pH > 7. Experiments were conducted to understand whether these different catalysts operate through a metal-based or radical-free mechanism, by measuring their selectivity, defined as the ability to discriminate between the possible reaction products. By virtue of their structural regularity, cyclohexane and adamantane were chosen as substrates to evaluate the value of the alcohol / ketone ratio and position 2 / position 3 ratio, respectively, following oxidation. The force constant of the eight catalysts, measured at specific pH values, was thus correlated with their selectivity. Interesting correlations were obtained following this approach. Furthermore, the dependence of the mechanism on pH was elucidated. In the end, we quantified the relative contribution of the metal-based and the radical-free mechanism to the global oxidation process by using specific hydroxyl radical quenchers (iso-propanol). We also attempt to define a relationship between the slope of a linear correlation of a family of ligands at various pH values and their relative metal-based and radical-free contribution.

Based on the discussed results, we propose the structure of possible catalysts which can provide efficient heterogeneous oxidation at the solid/water interface depending on the surrounding conditions (such as pH and substrates) of a reaction.

OM3

Electron exchange capacities of humic acid sorbed to redox active clays

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Iron (Fe) and Dissolved Organic Matter (DOM) are major drivers of biogeochemical redox processes in soils, sediments and aquifers. The redox reactivity of iron within clays was recently studied by using mediated electrochemical analysis.[1] Electron transfer processes upon sorption of DOM to redox active minerals are likely to occur but have not been studied in detail so far. Despite of their structural complexity, Fe-containing clays are suitable model systems to assess alterations in DOM redox properties upon sorption as they do not tend to release redox active Fe-species to the aqueous phase. In this work, we studied whether changes in the Electron Exchange Capacities (EEC) of DOM occur upon sorption to Fe-containing clays. Besides the potential fractionation and conformational changes taking place during DOM sorption, the electron transfer reaction between DOM and clays will likely affect the redox properties of DOM.

Sorption of Pahokee Peat Humic Acid (PPHA) to Na-rich montmorillonite (SWy-2, Fe content 2.3 % wt) was studied at pH 7 in batch experiments for several PPHA/clay ratios from low to high PPHA sorption. After pH equilibration, suspension aliquots were collected, and the rest was filtered using 0.45 µm membranes. Electron-Accepting and -Donating Capacities (EAC and EDC, respectively) were quantified for PPHA stock, the suspensions and the supernatants following mediated electrochemical analysis.[2]

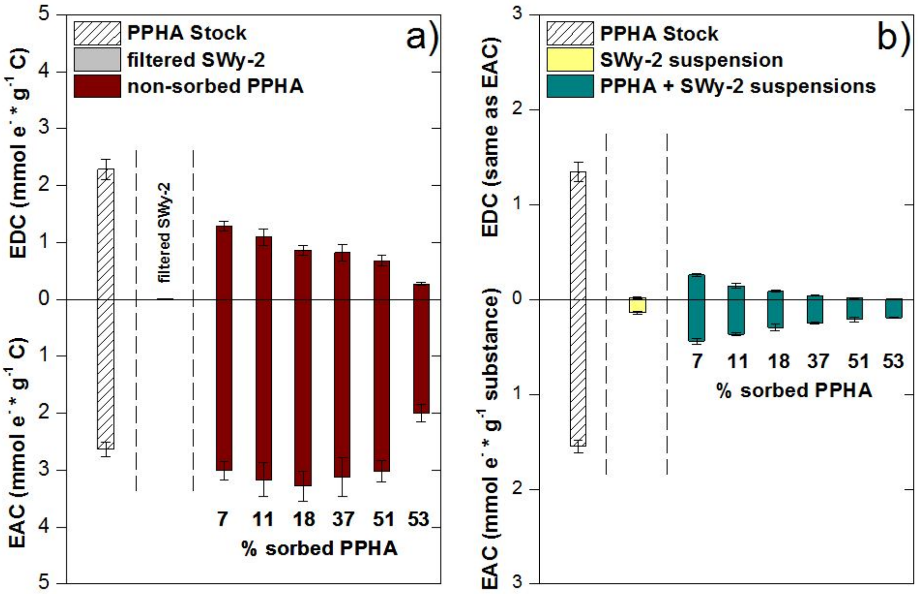

Figure 2: Electron-Donating (EDC) and -Accepting (EAC) Capacities of: a) Pahokee Peat Humic Acid (PPHA) and non-sorbed PPHA fractions normalized to carbon content, b) suspensions normalized to mass of substance in the sample. Substance indicates that EAC & EDC were normalized to mass of HA, mass of SWy-2 or total mass of PPHA + SWy-2 in sorption batch.

Figure 1a shows that EEC of non-sorbed PPHA fractions decreased up to 50 percent compared to PPHA stock solution, whereas it became more oxidized after electron transfer reaction with clay (up to 70 percent lower EDC). Suspensions containing PPHA + clay showed up to 80 percent lower EEC (normalized to total batch mass) compared to PPHA stock solution (**Figure 1b**). This effect was more pronounced with increasing amount of SWy-2 in the sorption batch (higher % sorbed PPHA). These results suggest that the electron transfer activity of DOM is greatly altered by sorption to redox active clay minerals.

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OM4

Morphology-dependent enhancement of arsenite oxidation to arsenate on birnessite-type manganese oxide

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Birnessite-type manganese oxide is a highly efficient oxidant and has been investigated widely for As(III) oxidation. Nevertheless As(III) oxidation rate is inevitably reduced due to favorable adsorption of coexisting ions and As(V) which passivate its surface. In this study, we explore a novel strategy to significantly improve As(III) oxidation performance by controlling birnessite morphology.The batch experiment results show that the nanoflower-like birnessite (Bir-NF) exhibits an incredible improvement in As(III) oxidation activity compared to nanowire-like (Bir-NW) and nanosheet-like (Bir-NS) birnessites. The morphology of birnessite varies from nanosheet to nanoflower not only promotes As(III) oxidation kinetics rate from 2.2×10^{-3} to 0.137 min^{-1} (Fig. 1a), but also reduces the adverse effect of adsorption of As(V) and coexisting ions on As(III) removal (Fig.1b). The origin of morphology-dependent enhancement of As(III) removal was experimen- tally and theoretically studied by As(V) adsorption on birnessites, phosphate adsorption kinetics, detec- tion of dissolved Mn2+ concentration, average Mn oxidation state, the point of zero charge, and density functional theory (DFT) calculations. The results reveal that significant enhancement of As(III) oxidation activity in Bir-NF as compared to Bir-NW and Bir-NS is attributed to its highly efficient contact between As(III) species and manganese oxide, as well as its fast charge transfer from As atom to Mn atom due to its highest oxygen vacancy defect concentration, thus significantly promoting As(III) oxidation activity.

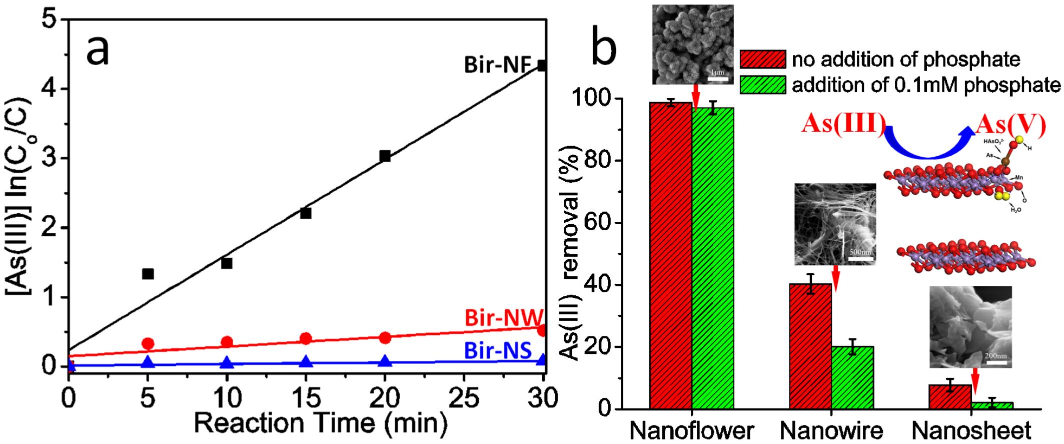

Fig. 1. The fitting result of As(III) oxidation on birnessites by a first-order kinetics equation (a) and arsenite removal before and after addition of 0.1 mmol L-1 phosphate:Experimental condition: 0.1 mmol L^{-1} As(III) and 0.6 g L^{-1} birnessite at pH 6.0.

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OM5

Zinc and Zinc-complexing ligands from rivers and anthropogenic activity in coastal South East Asia and around Singapore

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Organic complexing ligands dominate the chemical speciation of Zn in seawater, affecting its bioavailability and regulating its micronutrient role. Recent work indicates a connection between point sources related to marginal seas, riverine matter, benthic fluxes, and continental shelves, with ligand concentrations and binding strengths evolving along water mass trajectories.

We have been studying some of these processes in natural water samples in coastal South East Asia for the past 4 years. Here we present results from studies along a transect from South China Sea to Singapore to Malacca Straits, and a seasonal study around Singapore that investigate rivers and anthropogenic activity as sources of metals and ligands in and around agricultural and industrial anthropogenic influence in Singapore, Malaysia and Borneo. We obtained Zn ligand concentration and binding strengths using ASV, and Zn concentration using an NTA, isotope-dillution ICPMS method.

Results indicate that rivers are a large source of Zn ligands. Along the coastal transect there is a gradual trend of Zn ligands linked to rivers, more so in the narrow, more river-influenced Malacca Straits than in the wider South China Sea, where we hypothesize that ligands get dilluted. Around Singapore, a variety of sources of metals and ligands were studied, and we found excess Zn and Cd near fish farm and land reclamation impacted sites, and a response of ligands to cope with high Zn and Cd at a shipyard site. Monsoon seasonal variability and El Nino effect on riverine discharge are observed for Zn ligands at a site in the Singapore Straits. We have also studied mangroves as sources/storage of metals and ligands and found ligands related to those in the coastal waters. A comparison of these ligands will be presented to assess the relevance of each source of metals and complexing ligands to regulate regional and global distribution of ligands and bioavailable metal concentrations. Both L1 and L2 can be discerned in the region (logK’s ~11 and ~10), similar to those found in global water masses, corroborating our main hypothesis about riverine organic matter being related to Zn complexing ligands.

Further exploration into the storage and time-record of the metals and ligands in corals are shown in a separate presentation, where the method and preliminary results will be discussed.

OM6

Stability and reactivity of biogenic Mn oxides in the presence of natural organic matter

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The redox state of manganese in the environment is controlled by a complex synergy of abiotic and biogenic processes. Given the wide range of pore-water constituents (e.g., reactive oxygen and nitrogen species, organic acids, sulfide) that can transform manganese oxides, observed concentrations of manganese oxides within soils and sediments are likely a snapshot of a highly dynamic cryptic cycle. A better understanding of Mn redox cycling in natural systems is critical to predicting the cycling of both contaminants and carbon in soils. While Mn concentration has been cited as the "single main factor" controlling litter decomposition in forest ecosystems,[1] few studies have investigated the molecular-scale mechanisms of coupled oxidation-reduction processes between organic carbon and Mn oxides in the context of soil organic matter (SOM) dynamics.

In natural systems, biological precipitation is the major pathway for Mn oxidation and its subsequent precipitation as nanoscale, layer-type Mn oxides. The redox state of Mn influences Mn oxide structure and reactivity, modulating its capacity to accept electrons. Most studies quantifying Mn oxidation state have been conducted on abiotic oxides. The relative few studies that have characterized biogenic manganese oxides have been conducted in systems confounded by organic compounds, often HEPES buffer. Recently our group has shown that these buffers dramatically reduce the average manganese oxidation number (AMON) of abiotic oxides.[2] Biogenic oxides are similarly susceptible to reduction by organic buffers, the extent of which can be predicted by initial Mn(III) content. In this study, we investigate how the average manganese oxidation number (AMON), and thus the ability to accept electrons from organic compounds, differs between synthetic and biogenic Mn oxides introduced into natural matrices (e.g., forest soil, dissolved organic carbon). Average manganese oxidation numbers (AMON) were determined by $K\beta$ X-ray emission spectroscopy, X-ray absorption spectroscopy, and potentiometric titration. Pyrophosphate extractions were used to determine Mn(III) content of synthetic minerals.

Our results show that biogenic manganese oxides undergo significant reductive dissolution following the addition of wood extract, even in the presence of *P. putida,* a manganese-oxidizing bacterium. This increased Mn reduction relative to organic buffers (e.g., HEPES) suggests natural organic compounds present in pore-water are capable of a two-electron transfer reaction unlike organic Good buffers. The instability of Mn oxides in the presence of dissolved organic matter suggests that biomineral-assemblages are responsible for significant redox recycling of Mn which could provide a pathway for disproportionate turnover of organic carbon in soils and sediments relative to the observed concentration of Mn oxides.

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KN2

Ecocatalysis: An unsual combination of ecology and bio-inspired chemistry for tomorrow's chemistry

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Despite the enforcement of European regulations, the dissemination of metal trace elements in nature is evolving, while the depletion of mineral ressources is alarming. The aim of Ecocatalysis is the implementation of breakthrough innovation and cross-disciplinary research in ecological restoration, organic chemistry and green catalysis to overcome this paradox. Ecocatalysis focuses on the ecological rehabilitation of mining sites by phytoextraction, treatment of industrial effluents by remedial phytotechnology, named rhizofiltration. Based on the ability of specific plants to concentrate metals, we address the transformation of plant-derived transition metals to green catalysts. The structure, activity, selectivity and recyclability of ecocatalysts are showcased in selected reactions, such as oxidations, reductions and coupling reactions.

The concept of Ecocatalysis provides catalytic and ecological tools for tomorrow's chemistry, based on the recycling of primary and strategic metals to create scientific and economical values. It offers pioneering solutions to initiate an unprecedented program in green catalysis.

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Tuning the injection and immobilization of reactive nanoparticles in the aquifer for an effective site remediation

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Nanoremediation, consisting of the subsurface injection of a reactive colloidal suspension for the in situ treatment of contaminated aquifers, is an innovative and effective remediation technology. Despite the evidence of its effectiveness obtained in recent years, still some relevant issues need to be solved to promote a wider application. Among these issues, a critical one is the effective delivery and the appropriate dosing of the nanoparticles into the subsoil for the correct emplacement of the in situ reactive zone. Correct nanoparticle distribution in the aquifer minimizes the overall cost of the reclamation as well as the potential secondary risks associated to the uncontrolled migration of the injected particles.

In this study, a model-assisted strategy, NanoTune, is developed to control the distribution of colloids in saturated porous media. The proposed approach consists of the sequential injection of a stable suspension of reactive nanoparticles and of a destabilizing agent with the aim of creating a reactive zone within a targeted portion of the contaminated aquifer. The controlled and irreversible deposition of the particles is achieved by inducing the mixing of the two fluids in the desired portion of the aquifer.

This approach is here exemplified by the delivery of humic acid-stabilized iron oxide nanoparticles (FeOx), an innovative reagent for the in situ immobilization of heavy metals. Divalent cations, which are known to cause rapid aggregation of the suspension because of their strong interaction with the humic acid particle coating, are used as destabilizing agents. The injection strategy is here applied in 1D columns and 2D setups to create a reactive zone for heavy metal removal in the central region of the sandy bed. The controlled deposition of nanoparticles at the desired location is achieved by tuned sequential injection of pulses of a particle suspension, a solution of divalent cations (used as destabilizing agent), and water (used to separate the two interacting fluids). The two fronts, which advance at different rates, overlap at the target location, where the particles deposit and accumulate irreversibly, creating a reactive zone. A transport model was used here to assess the correct sequence and duration of the injection of the different solutions.

The strategy, developed using FeOx, can be generalized and extended for application to any other colloidal suspensions, provided that a suitable destabilizing agent is first identified. Such further examples are briefly presented. The approach proposed in this work represents an important step forward in the field of nanoremediation, since for the first time it is possible to achieve control on the short- and long-term distribution of engineered particles upon injection.

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OM8

Daphnia magna filtration efficiency and mobility in sheared flows

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Daphnia magna are filter feeder organisms that prey on small particles suspended in the water column[1]. Since *Daphnia* can feed on wastewater particles, they have been recently proposed as potential organisms for tertiary wastewater treatment[2,3]. There are many studies that demonstrate that *Daphnia* reduce their activity when subjected to unfavourable environmental conditions[4]. *Daphnia* have been found to exhibit disorders in filter feeding activity, swimming speeds and trajectories, growth, heartbeat, metabolism and survival when exposed to unfavourable factors[5]. Hydrodynamics might impose some limitations to the normal functioning of Cladocera. An increase in *Daphnia* swimming speed along more tortuous paths, resulting from the chaotic movement of the flow, occurred after turbulence was increased using an oscillating grid[6]. However, analysing the effects of hydrodynamics on *Daphnia* filtration in sheared flows have scarcely been studied. Despite all the studies on how individual factors or combinations of them affect *D. magna* performance, how the flow environment affects their filtration rate is hardly known and is crucial element when determining the flow rate in any reactor designed to treat water based on *D. magna* filtration. This study focuses then, on quantifying both the filtration efficiency and swimming velocities of *D. magna* under different hydrodynamic conditions.

A total of 72 experiments were designed to determine the favourable hydrodynamic flow environment for *D. magna* performance. Filtration capacity and swimming speed were used as the main parameters to study the responses of *D. magna* to the hydrodynamics of the flow. Two devices were used to study the performance of *D. magna*, an oscillating grid and a Couette flow device. The oscillating grid provided a homogeneous pure turbulent flow whereas the Couette device presented a mean flow that can be laminar or turbulent[7]. Different flow velocities and turbulent intensities were studied. Both filtration and *Daphnia* movement responded differently if the flow was laminar or if it was turbulent. In a laminar-dominated flow regime *Daphnia* filtration was enhanced up to 2.6 times that of a steady flow. In contrast, in the turbulent-dominated flow regime *D. magna* filtration was inhibited. In the laminar flow regime *Daphnia* moved freely in all directions, whereas in the turbulent flow regime *Daphnia* were driven by the streamlines of the flow. A model based on *Daphnia*-particle encountering revealed that the filtration efficiency in the laminar regime was driven by the length of the *D. magna* and the shear rate imposed by the system.

Therefore, all the hydrodynamics have to be considered in the design of an environmental-friendly wastewater treatment system based on *D. magna* filtration, which might be potentially used as a tertiary treatment.

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OM9

TiO_x reactive electrochemical membranes for the removal of organic pollutants from water: process and material optimization

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Introduction: Anodic oxidation (AO) is a promising electrochemical advanced oxidation process for water treatment based on both direct electron transfer and generation of hydroxyl radicals (•OH). •OH are produced in a heterogeneous way in the electrochemical cell, therefore, new approaches are necessary in order to break the high cost bottleneck related to the limited mass transfer of organic pollutants from the bulk to the electrode surface [1]. In this study, TiO_x reactive electrochemical membranes (REM) synthesized from carbothermal reduction of TiO_2 are used for the mineralization of biorefractory pollutants during filtration operation [2].

Methods: Experiments were performed using a cross-flow filtration setup in inside-out or outside-in mode. TiO_x REM were used as anode (40% porosity, median pore size = 1.4 µm) while stainless steel (inside-out mode) or carbon felt (outside-in mode) was used as cathode. Paracetamol (PCT) was selected as model organic compound. The use of TiO_x REM with lower pore size and different Magnéli phases (1.75 (Ti_4O_7) < x <1.80 (Ti_5O_9)) was also investigated. Voltage, permeate flow, [PCT], total organic carbon, mineralization current efficiency and energy consumption were monitored.

Main results and discussion: PCT oxidation rate was assessed during filtration through the TiO_x REM n inside-out mode (figure 1). For example >99% degradation and 97% mineralization of 0.18 mM of PCT were observed after a single passage through the REM (Permeate flux = 150 $L\ h^{-1}\ m^{-2}$; i = 15 $mA\ cm^{-2}$). Mineralization current efficiencies were in the range 10 – 50% according to operating conditions. The high efficiency is explained by both the high electro-catalytic reactivity of TiO_x and the convection-enhanced mass transport of pollutants, compared to the use of conventional plate electrodes. The influence of current density, permeate flux and pollutant concentration were studied. These parameters have a strong influence on crucial phenomena such as electro-polymerization and oxygen evolution reactions. The influence of REM pore size on process efficiency was analyzed by taking into consideration diffusion and convection mass transport phenomena inside REM pores. Besides, the influence of the nature of Magnéli phases synthesized was studied as regards to the electro-catalytic reactivity of the REM.

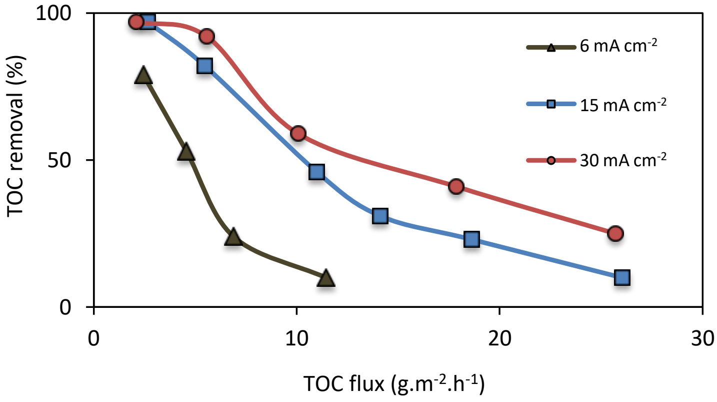

Figure 3: Total organic carbon (TOC) removal (%) after a single passage of the solution through the REM in inside-out mode as a function of current density and TOC flux (TOC flux = Permeate flux × $[TOC]_0$). Experiments were performed at constant initial PCT concentration ($[PCT]_0$ = 0.18 mM) and increasing permeate flux.

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OM10

Fast elaboration of chitosan porous beads by prilling and selective adsorption of heavy metals by complexation

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Chitosan (CS) gel beads of milimetric size were produced by an electromagnetic laminar jet breakup technology also known as "prilling". The used equipment allows users to quickly produce sufficient amounts of material for a subsequent industrial scale up. Ionic imprinting technique was used to modify the beads in order to increase their adsorption selectivity towards dicationic heavy metals (copper (II), nickel (II) or cobalt (II)). Sulfate and chloride salts of these cations were used as templates. The optimized "ion template" concentrations (5 to 10 % wt. of CS) allowed us to obtain chitosan solutions with reduced Newtonian viscosities enabling the prilling process, and yielding to hydrogels having higher storage moduli than non-imprinted ones and hence lyophilisated beads with high mechanical strengths. This technique has allowed us to design spherical and monodispersed beads. The template leaching step, which is of a great importance when using the imprinting processing route, was also optimized and fully desorbed beads were obtained after acid washing (**Figure 1**).

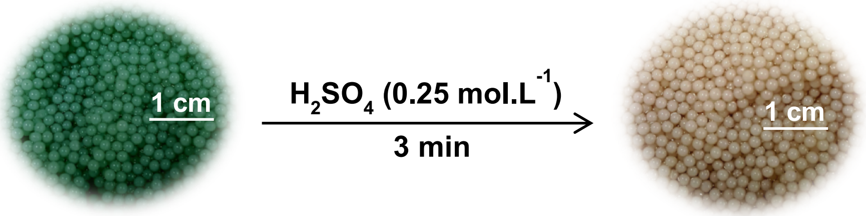

Figure 1. Chitosan beads imprinted with nickel chloride, before and after the leaching of the template in presence of H_2SO_4

Adsorption kinetics were studied for the non-imprinted chitosan beads (NI-CS) and for the imprinted ones (I-CS) at low metal ion concentrations (400 µg.L^{-1}). The maximum adsorption capacities of the prepared beads were then determined by isotherm studies. The imprinted chitosan beads were shown to be more selective and efficient adsorbents having higher adsorption capacities and reduced equilibrium time (**Figure 2**) than the non imprinted ones, prepared in the same conditions. Their porosities were analysed and compared by measuring their specific surface areas and by scanning electron microscopy observations.

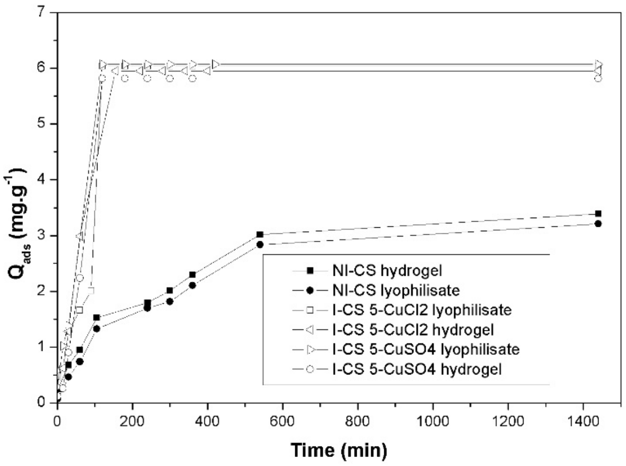

Figure 2. Kinetic adsorption curves of copper (II) by imprinted and non-imprinted chitosan beads in forms of hydrogels and lyophilisates. ($V_{solution}$ = 0.5 L, m_{CS} = 0.033 g, Ci = 0.400 µg.L^{-1})

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Treatments to degrade polybrominated diphenyl ethers in water and their feasibility to contaminated soil

OM11

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Polybrominated diphenyl ethers (PBDEs), one of emerging environmental contaminants, have been widely used as additive flame-retardants in various products to reduce their fire hazards by interfering with the combustion of the polymeric materials. However, some PBDEs were identified as endocrine disruptors (Darnerud et al. 2001), and PBDEs were found in human blood, milk, and tissue (Hites 2004). Since PBDEs were widely detected in the environment, the public concern about the risks of PBDEs has increased in the world. The major PBDE product is decabromodiphenyl ether (DBDE or named BDE-209). Due to its extreme hydrophobicity and the largest number of bromine atoms, DBDE will accumulate in organisms (Schecter et al. 2004). Some treaments of PBDEs were developed in the recent years and discussed.

We observed the quick photodegrdation of PBDEs especially DBDE under sunlight in Taiwan (Shih and Wang 2009). A linear increase of the photodegradation rate constant for DBDE was observed with the solar light intensity. The degradation reactions follow the pseudo-first-order kinetics. The photodegradation of DBDE produced other less brominated diphenyl ethers under ultraviolet light exposure, suggesting that the photodegradation of DBDE is a sequential dehalogenation mechanism. Under strong and enough sunlight, PBDEs can be fast degraded. However, the penteration of light into water and soil is limited. We also investigated the debromination of PBDEs with zerovalent iron and micorbes.

The chemical reduction kinetics of DBDE by nanoscale zerovalent iron (NZVI) is much faster than that of commercial microscale zerovalent iron (MZVI) (Shih and Tai 2010). The first-order rate constant of NZVI is about 7-fold higher than that of MZVI. The surface area normalized rate constant of NZVI is similar to that of MZVI indicating that the increased reactivity of the NZVI is mainly attributed to the higher surface area of the NZVI. In different pH conditions, different kinetics and efficacy were found. Overall, adsorption on NZVI plays a role on the removal of DBDE due to the (hydro)oxides formed on NZVI after reactions. Furthermore, the removal processes of DDBE with MZVI were investigated over a long-term (Peng et al. 2013). The removal kinetics revealed two-step kinetics: surface adsorption of PBDEs on MZVI dominates the removal mechanism in the beginning and further debromination with MZVI was found. Finally, about 70% of DBDE was degraded by MZVI within about one month. Since common ions in water affect the reactivity of NZVI (Tso and Shih 2015), the carboxymethylcellulose modofed NZVI can overcome this issue and be stable in water (Tso and Shih 2017).

Although we found some microbes to degrade low-bromianted BDEs (Chen et al. 2010, Shih et al. 2012a), we cannot find any strains to degrade DBDE in Taiwan until now. With the combination of MZVI, microbial community in an anaerobic sludge can degrade DBDE (Shih et al. 2012a, Shih et al. 2012b). In this co-incubation, the enhancement of removal ability when compared to the single component conditions was found. Although microbes could hinder the accessibility of MZVI to DBDE and reduce the removal ability in the initial stage, the existence of reducing-bacteria and hydrogen-bacteria enhanced the degradation ability of MZVI, indicating microorganisms contribute to enhance the degradation ability of MZVI.
Since we also observed plant uptake of PBDEs from soils (Yang et al. 2017), one farm contaminated with PBDEs should be remediated. The possible soil remediation will be discussed.

Although some treatments such as quick debromination of PBDEs by photodegrdation and reduced metals such as NZVI, slow degradation through soil microorganisms, as well as the combination of microorganisms and reduced metals in water were studied, the application of these technologies in PBDE contaminated soil site is still needed to be discussed since crop uptake of PBDEs from soils were found, which could casue food safety issue.

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OM12

Boron removal by selective and anionic resins from batch and column experiments

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Boron is an essential nutrient for living organisms, especially for plants where it is involved in cell wall composition. But boron excess can cause some problems on the plant development, on humans and animals. Boron toxicity also changes blood composition, caused disorder in neurological, physical, intellectual development.

Nowadays, due to the shortage of fresh water sources, seawater desalination has been becoming an alternative fresh water supply. However, the presence of boron in seawater is quite high (4.5 mg L^{-1}; 0.42 mmol L^{-1}). Therefore, the World health Organization has recommended a guideline of 0.5 mg L^{-1} B (46 µmol L^{-1}) in drinking water and a maximum limit of 0.3 mg L^{-1} B (28 µmol L^{-1}) in fresh water used for irrigation[1].

The objective of this work was to study the mechanisms of boron surface exchange on different materials versus time and at equilibrium depending on some physicochemical parameters such as pH, initial boron concentration, reaction time in order to find a new exchanger for boron removal.

Boron removal was carried out by ion exchange process using two types of resins: Amberlite IRA 743, Diaion CRB 03 as boron selective resins with methylglucamine functions; and Ambersep 900-OH and Amberlite IRA 402 Cl as anionic exchange resins with ammonium functions.

From batch studies, fast exchange between resin surface and liquid phase was observed. At equilibrium, experimental results showed that the maximum adsorption was observed to be achieved at pH 8 for Ambersep 900-OH and independent on pH range from 6 to 12 for Amberlite IRA 743. In the range of boron concentrations studied, (i) the Langmuir-type relationship was applied to the Ambersep 900-OH and Diaion CRB 03 resins for fitting the maximum sorption capacity and the Langmuir-type coefficient which are 2.2 and 0.87 mmol g^{-1} respectively; (ii) the BET-type relationship was used for describing the boron behavior in the presence of the Amberlite IRA 743 resin and for estimating the BET-type coefficient and the boron sorption capacity (0.43 mmol g^{-1}); and (iii) the Henry-type model was used for fitting boron sorption behaviour in the case of the Amberlite IRA 402 Cl.

Column experiments were performed with the anionic resin Ambersep 900-OH and the selective one Amberlite IRA 743 by studying both the influence of boron concentration, pH and the residence time. For the selective resin, Amberlite IRA 743, if the residence time decreases, the boron breakthrough is fast followed by a long tail. For larger residence time, local equilibrium seems to be assumed. Results are thus consistent with batch experimental data. For the anionic resin, the non-linear behaviour is also confirmed. Moreover, column experiments showed a strong difference during desorption. To regenerate resins, acid and basic treatments are necessary for the selective resin although a basic solution is enough for the anionic resin.

Optimized models and non-linear models were studied to build up an exchange model for predicting boron fate.

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KN3

The effect of humic colloids on the fate of organic contaminants and engineering nanoparticles in the environment

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Humic colloids including soil organic matter (SOM) play a key role in the environmental security on earth since it provides many functions in agricultural and soil sciences such as the retention of water and nutrients, formation of soil structure, etc. In this talk, its many other important abilities will be presented in views of environmental organic chemistry and environmental nanotechnology. For environmental organic chemistry, sorption kinetics and capacities of organic contaminants such as volatile organic compounds (VOCs) in SOM affect the fate of these pollutants in soils. To understand the sorption/desorption of VOCs from humic substances [1, 2], the time courses of toluene sorption to compressed humic substance disks were investigated. The apparent diffusivity of VOCs with humic substance disks ranges from 10^{-8} to 10^{-9} cm^2/s after simulated by use of a diffusion model. Furthermore, molecular dynamics simulations, a computational technique, have been successfully used to study the sorption kinetics of organic contaminants in SOM [3, 4]. This technique may provide an alternative method to reliably estimate dynamical properties of contaminants in humic substances.

The intrinsic sorption kinetics of toluene in clay or humin films was investigated under dry and humid conditions [5]. The time scale for intrinsic vapor sorption without mass transfer hindrance is less than a few minutes within these thin films. Higher intensity of sorbed toluene was found on Cu-form than on Ca-form under the dry condition, which indicates stronger interaction occurring in dry Cu-montmorillonite. On montmorillonites some portion of toluene was desorbed at an extremely slow rate under the dry condition. Some newly identified peaks were persistent against desorption from Cu-montmorillonite, suggesting the existence of irreversibly sorbed species and the possibility of transformation of toluene occurring in clay systems.

The soil organic-mineral compositional heterogeneity complicates the transport and fate of VOCs in soils. In our previous study [6], the sorption kinetics of toluene vapor in soils can be explained by a two-stage sorption phenomenon. The first stage is reflective of surface adsorption and the second stage of much slower partitioning into SOM. The relative contributions of these two stages to soil uptake can be quantifiable by two independent parameters, the soil organic fraction and the surface area.

In the real environment, water molecules cover all the sorption sites on soil inorganic fractions and only SOM plays an important role in the removal of organic contaminants from water. Recently, soil organic fractions not only SOM but also carbonaceous materials such as black carbon (BC) are included into the sorption of organic contaminants. Furthermore, a linear solvation energy relationship (LSER) approach was used to investigate the evolving contributions of intermolecular interactions controlling organic compound sorption by granular activated carbon as a surrogate of BCs from water as a function of sorbate chemical activities [7]. Several developed LSER equations are useful for estimating equilibrium sorption coefficients for new sorbates of interest.

In the field of environmental nanotechnology, nanoparticle (NP) powders are easily aggregated once they enter into water [8]. The effects of electrolytes on the aggregation of different NPs including stabilized commercial NPs were evaluated [9-11]. Not only the aggregation of NPs but also humic substances could decrease the possible toxicity caused by NPs. On the other hand, many NPs have been developed to remove contaminants from the environment, e.g. nanoscale zerovalent iron (NZVI). NZVI has applied in the field treatments and can degrade many emerging contaminants [12, 13]. Humic colloids could stabilize NPs in water and facilitate their transport in the subsurface to remove contaminants.

Since SOM provides a good shelter and food supply for microbes, soil microbial community can degrade many organic contaminants, e.g. bisphenol A, one emerging contaminant [14]. On the other hand, plants can uptake organic contaminants from soils [15], which could cause a food security issue; however, SOM can retain most of these contaminants in soils to prevent their translation into crops. SOM, the God-given treasure, prevents negative effects on humankind after humans create a lot of environmental pollutions.

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OM13

Effects of mixing intensity on the flocculation kinetics of colloidal particles

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Evaluation of mixing intensity by means of the rate of salt-induced of rapid coagulation that is equivalent to collision frequency of polystyrene latex (PSL) particles were revisited to clarify the applicability of normalizing method of colloid mixing which is frequently encountered in engineering application. Experiments were carried out using a small mixing vessel (40ml) equiped with Rushton stirrer for the dispersion of PSL particles with different diameters as a function of mixing intensity. We confirmed that under the condition of high mixing intensity, measured rate of coagulation follows the theoretical prediction in which $(dN_t/dt)/N_0 \sim a_0^{2.46}$. However, in the region below 200 rpm, the dependency of the rate on the particle size is found to be lower than the value of theoretical prediction (**Figure.1**).

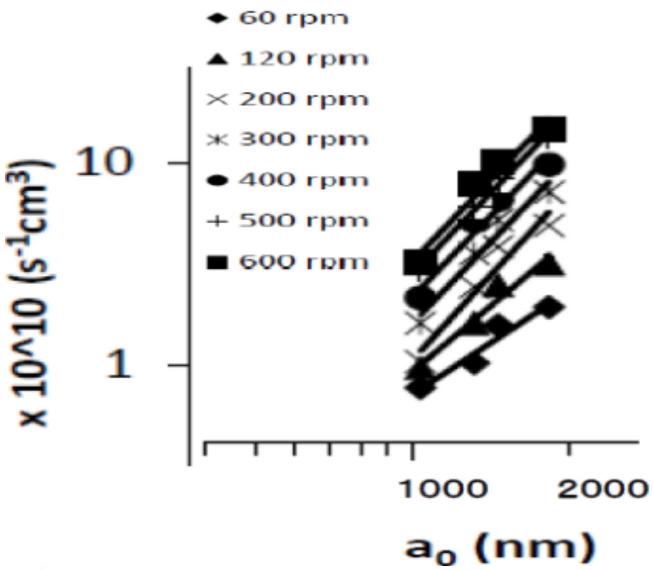

Figure 4: The reduced rate of turbulent coagulation as a function of the diameter of primary particles.

The result obtained from salt-induced coagulation was applied to analysis of flocculation induced with polyelectrolyte. Rate of flocculation induced by polyelectrolyte in initial stage was confirmed to be faster than those of coagulation induced by salt. For the evaluation, we used an index of β defined as,

$$\beta = \frac{\text{rate of flocculation}}{\text{rate of salt induced rapid coagulation}}$$

The value of β was found to be a function of mixing intensity taking maximum around 200 rpm (Table 1). The result implies at least two limiting factors in the region of low Pecret number.

Table 1. The value of β as a function of mixing intensity.

Mixing intensity (rpm)	60	120	200	300
β	3.24	3.54	3.74	3.11

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OM14

Ion and particle foam flotation for aqueous phase remediation

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The process called ion flotation allows to concentrate ions or other charged entities from an aqueous solution within a foam that can be produced at the top of the solution. Foam is created by introducing gas bubbles in the solution that contains surfactant molecules at very low concentration (close to CMC).To maintain a high foam stability in order to limit the solution transport within the foam thanks to an efficient drainage, some specific foaming agents have to be used. Multifunctional surfactants such as AKYPOs or ETHOMEENs, both being pH-sensitive and containing ethylene oxide groups are good candidates because they can interact with multicharged ions without precipitation. We have shown in previous studies that monovalent cations are much more depleted from the foam films than divalents or even trivalents and thus are difficult to concentrate using this type of foam flotation.

In the scope of nuclear incident on the Fukushima power plant in Japan soils remediation contaminated by radiactive ceasium became a mission of great importance. Prussian blue and its analogues (PBA) represent a class of materials which is well established for the selective sorption of the heavy and radioactive metals such as caesium and thallium [1-3]. We have shown that ceasium cations can be removed from solution via first their sorption in PBA nanoparticles that can be synthesized in situ the solution and then through the flotation of the nanoparticles (Fig. 1 – left and middle). Size and surface properties of the nanoparticles along with the surfactant chemistry are main parameters determining the efficiency of decontamination process in this procedure. Caesium can be efficiently removed from aqueous solution, down to the ppb level..

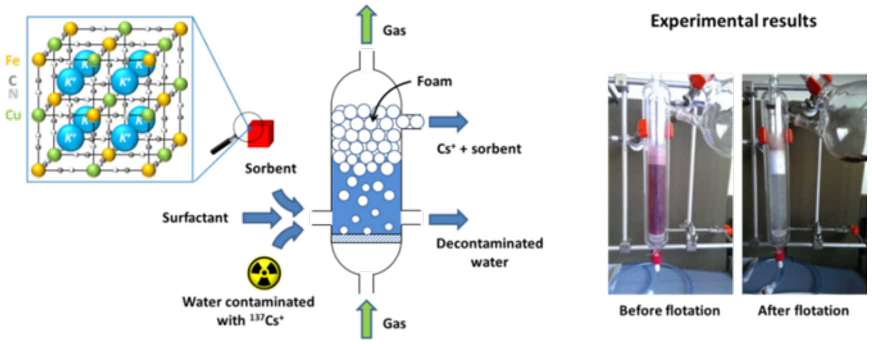

Figure 5: left – local structure of Prussian blue analog nanoparticules that can be synthesized in-situ of the flotation column; middle - pictures of flotation column; right- two pictures of the column before and after the flotation of the PBA-NP charged with caesium cation that were previously dissolved as chloride form in the solution.

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OM15

Simulation of unsaturated clay pores at the microscopic scale

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Numerous experimental and theoretical studies have focused on predicting the performances of clay minerals as barrier materials in the containment of high-level radioactive waste by evaluating the diffusion of mobile species in compacted, water-saturated Na-bentonites. However, storage conditions are sometimes unsaturated as in the ANDRA's Cigéo[1] deep storage center. Calculation codes used to study the reactive transport of species at the scale of the storage structures are based on data obtained experimentally or theoretically and because of the amount of data available, they describe rather well the saturated clay pore systems. On the other hand, available data becomes more sparse in the case of unsaturated pores. Yet, the unsaturation can deeply modify properties such as species distributions and diffusion coefficients. Thus, microscopic studies of unsaturated pores are necessary in order to implement the unsaturated case in reactive transport codes[2].

In the present work, we choose to study unsaturated pores of Na-montmorillonite and Na-illite, which are the main minerals in the clay media chosen by ANDRA for the Cigéo project . Because of the negative charge of their aluminosilicates sheets, there is an overconcentration of cations at the surface of the clay layers and anions are partially excluded from the interlayer space. This distribution is more or less well described in the case of the saturated pore with the double layer model but has been little studied in the unsaturated case. Therefore, we explore the evolution of the double layer and the structure of the mobile species at the solid/liquid interface in the presence or absence of salt as a function of the unsaturation. The impact of the unsaturation on the mobility of mobile species was also studied. These properties are calculated on the microscopic scale by Molecular Dynamics simulations in order to validate macroscopic laws or, if necessary, to propose new ones that could be integrated in a mesoscopic code such as calculation codes mentioned earlier. Finally, because the system presents two interfaces, a solid-liquid interface and a liquid-gas interface, we are comparing the results between a reference non-polarizable force field, CLAYFF[3], and a polarizable force field that should better take into account the phenomena at the interfaces[4,5]. For the latter, we chose to use PIM[6], a new force field currently in development at PHENIX laboratory.

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Charge properties of TiO_2 nanotubes in $NaNO_3$ aqueous solution

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Specific and often enhanced properties of TiO_2 nanotubes make them suitable for various application such as adsorbents for decontamination of different organic molecules and heavy metal ions. Furthermore, TiO_2 nanotubes can be used for degradation of environmental pollutants by exploiting its photocatalytic properties or even as carriers of various matter in a nanomedical application [1]. The majority of applications are conducted in aqueous media. Therefore, in order to understand and to successfully manipulate the mentioned processes, it is crucial to gain insights into charging phenomena of TiO_2 nanotubes. In this article, the surface charge properties of titania nanotubes in $NaNO_3$ solution were investigated through electrophoretic mobility and polyelectrolyte colloid titration measuring techniques. In addition, we used HR-TEM imaging to determine the morphology of TiO2 NTs. A theoretical model based on the classical Density Functional Theory coupled with the charge regulation method in terms of mass action law was developed in order to understand the experimental data and to provide insights into charge properties at different physical conditions, namely pH and NaNO3 concentration.

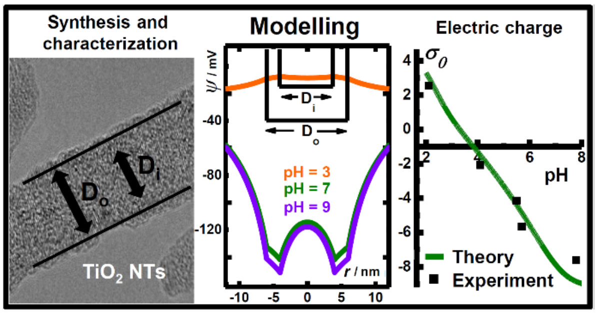

Figure 6: Schematic representation of step-by-step development of a simple but predictive theoretical model

Two intrinsic protonation constants and surface site density have been obtained. The electrostatic properties of the system in terms of electrostatic potentials and ion distributions were calculated and discussed for various pH values. The model can quantitatively describe the titration curve as a function of pH for higher bulk salt concentrations and the difference in the equilibrium amount of charges between the inner and outer surfaces of TiO_2 nanotubes. Calculated counterion (NO_3^-) distributions show a pronounced decrease of NO_3^- ions for high bulk pH (both inside and outside of TiO_2 nanotubes) due to the presence of the strong electric field. With the decrease of bulk pH or the increase of the salt concentration, NO_3^- are able to accumulate near the TiO_2 nanotubes surfaces [2].

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Acknowledgement - The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement no. [320915] "REE-CYCLE": Rare Earth Element reCYCling with Low harmful Emissions. The authors thank the Research Agency for support through grant BIFR/ CEA/16-18-002 and the Slovenian Research Agency for support through program P3-0388.

OM17

Vapor pressure and Aqueous solubility measurements of phthalates and phenols contained in recycled food packages

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In recent times, the use of recycled materials for packaging has undeniably been intensified. Nevertheless, recycling systems could not effectively eliminate the potential organic contaminants (alkyl phenol, phthalates, aldehydes, etc.) existent in such packages [1].

The migration process and/or the ability of these contaminants to be absorbed into the recycled material, subsequently released by the packaging material, and then trapped by the matrices they contain, has become a potential source of exposure to consumers [2].

This migration process is controlled by the nature of the packaging, time, temperature, and the physicochemical properties of the contaminant. The literature suffers from a lack of data related to the physicochemical properties (Vapor pressure, aqueous solubility) of these contaminants[3].

In this work, we studied the vapor pressure of 4-n-octylphenol (4-n-OP) as a function of temperature using the dynamic gas saturation apparatus between 298.15 K and 328.15 K and values ranged from 10^{-2} to 10^{3} Pa. Likewise, we studied the aqueous solubility of dipentyl phthalate (DnPeP) using the dynamic saturation method (DCCLC) in a range of temperatures between 298.15 K and 303.15 K where values ranges in 10^{-8} mol fraction.The analyses are performed by UHPLC-DAD using external calibration curve for both chemicals. These experimental data are often non-existent in the literature for the majority of the contaminants identified in the packaging materials.

These properties will enable the calibration of any state equation or molecular modeling in a context of constant concern to combine the search for quality experimental measurements with the development and validation of models.

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Surface structure of Ferrihydrite in relation to surface energetics, chemical stability, and competitive oxyanion adsorption

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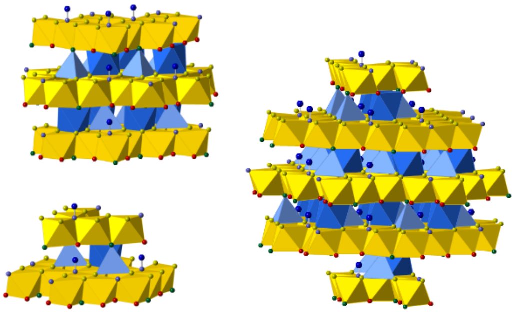
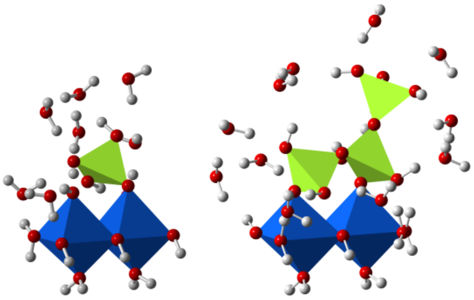
Fe (hydr)oxides are of great importance in nature, science, and technology. Ferrihydrite (Fh) is chemically the most stable Fe(III) (hydr)oxide at the nanoscale due to its exceptionally low surface Gibbs free energy (0.186 J m^2) as a result of Fe-surface depletion changing the polyhedral composition of the surface compared to that of the mineral core [1].



Surface depletion of Fe affects many properties of Fh, such as the ratio of edge-to-corner sharing ratio of the Fe polyhedra of the Fh material [2], in excellent agreement with high-energy total X-ray scattering data [3], the dehydration without structural decomposition [4], the molar mass, mass density, and water content as found experimentally [5], as well as ferrimagnetism [6], all being highly particle size dependent. Surface depletion may also occur in other Fe oxides such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3).

Elucidating the surface structure of the Fh family (Figure 1 with *d* ~ 1.5 - 2.3 nm) provides insight in the various types of reactive groups and their surface site densities, being crucial for the development of a mechanistic surface complexation model based on the concept of charge distribution [2]. The CD model parameterized for Fh enables the evaluation of the competitive oxyanion (PO_4, AsO_4, SiO_4) adsorption behaviour in engineered and natural systems which will be illustrated [7].

For Fh systems with silicate, CD modeling reveals a surface speciation with monomeric and polymeric Si (Figure 2), in agreement with recent differential PDF analsyis [8]. H-bonding occuring within the monomeric Si complex will be discussed in relation to the interfacial charge distribution. The model describes a whole suite of data comprising pH, electrolyte, and ion concentration dependency can be described, as well as the competition with As(III), As(V,) and P(V). This is highly relevant for practical applications of Fh [9] preventing e.g. leaching of PO_4 or reducing the bioavaliability of PO_4 in case of nature restauration. However, crucial in these applications is also the modeling of adsorbed organic matter [10].



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OM18

Arsenate uptake by fresh and aged Fe oxidation products

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The oxidation of dissolved Fe(II) in aerated water results in the formation of amorphous to poorly-crystalline Fe(III)-precipitates that profoundly impact the fate of nutrients and contaminants in aquatic and terrestrial systems. Phosphate (P), silicate (Si) and Ca strongly influence the structure of fresh Fe(III)-precipitates and arsenate (As(V)) uptake as well as the transformation of fresh Fe(III)-precipitates and concomitant As(V) retention or release.

We quantified the interdependent effects of P, Si and Ca on the composition and structure of fresh and aged Fe(III)-precipitates and the co-transformation of arsenate [1-3]. Precipitates were synthesized by oxidation of 0.5 mM Fe(II) at P/Fe ratios from 0 to 2 in aerated 8 mM bicarbonate-buffered (pH 7.0) electrolyte containing 7 µM As(V), with 8 mM Na, 4 mM Ca, 4 mM Mg or 7 mM Na + 0.5 mM Ca as electrolyte cations. Additional experiments in Na and Ca electrolytes were performed in the presence of 0.5 mM Si. After complete Fe oxidation and precipitation (4 h), filtered and unfiltered solutions and fresh precipitates were collected for analysis by ICP-MS and Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. In the aging experiment, the fresh precipitate suspensions were transferred into an oven and aged for 30 d at 40°C. The evaluation of the Fe K-edge EXAFS spectra of fresh and adge precipitates revealed gradual variations in the structure of the solids that could be described in terms of five endmembers: (i) poorly crystalline lepidocrocite (electrolytes without Si) or (ii) silicate-containing ferrihydrite (electrolytes with Si) formed in the absence of phosphate, (iii) amorphous Fe(III)-phosphate or (iv) Ca-Fe(III)-phosphate formed at high P/Fe ratios, and (v) ferrihydrite/hydrous ferric oxide (Fh/HFO) formed by the transformation of (Ca-)Fe-phosphate. The transformation of Fe(III)-phosphate into a ferrihydrite-type precipitate was the most pronounced structural change during aging. In addition, a small increase in the crystallinity of poorly crystalline lepidocrocite and in the polymerisation of the ferrihydrite-type precipitate fraction was observed.

Depending on initial P, Si and Ca concentrations and thus precipitate type, dissolved As(V) concentrations in the fresh precipitate suspensions varied by up to 3 orders of magnitude. During aging, substantial As(V) release was observed in the absence of Ca and Si. In combination, the presence of Ca and Si led to more effective P and As(V) uptake by fresh precipitates and substantially reduced P and As(V) remobilization during aging.

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OM19

Heavy metals sorption from industrial effluents using biogenic iron compounds

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Heavy metals are present in wastewaters from industries such as electroplating, mining, metal processing, or petroleum refinery [1]. The treatment of these effluents is attracting growing interest due to environmental and health issues, and increasingly restrictive regulations. Microbial iron compounds can be a cheap source of adsorbents. Many ferric iron mineral surfaces are positively charged at neutral pH due to their high points of net zero charge. These biomaterials can be good adsorbents for negatively oxyanions of toxic metals like arsenate, arsenite or chromate [2]. The objective of this work was the study of heavy metals sorption from electroplating wastewaters (Industrial Goñabe (Spain)) using the nanometric iron compounds generated by a natural consortium from an abandoned mine.

The microbial consortium was grown under anaerobic conditions with lactate and soluble ferric citrate generating a precipitate. This precipitate was identified as a mixture of siderite ($FeCO_3$) and iron oxides, mainly magnetite (Fe_3O_4) (Fig. 1A). Then, the iron compounds were encapsulated in alginate beads, which could be used in column experiments (Fig.1B).

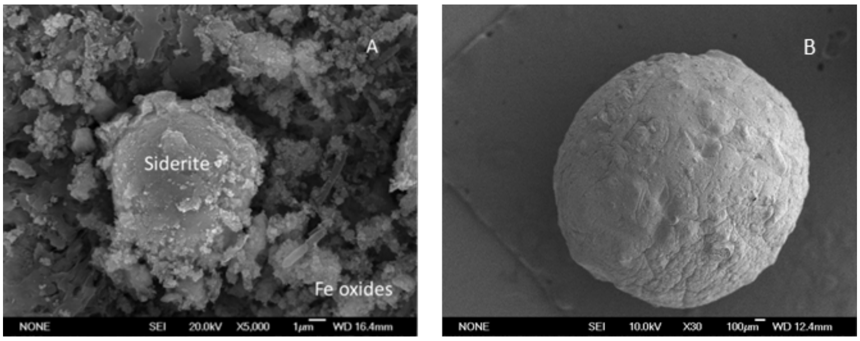

Figure 7: SEM images of iron compounds generated by the microbial consortium and (b) iron compounds in alginate beads.

The electroplating wastewaters were characterized (pH 2.2; [Cr] = 2064 mg/l; [Zn] = 306.4 mg/l). The adsorptive properties of the iron compounds were studied considering variables, such as pH values and metal concentration. The optimal pH value for metal uptake was pH 4. Biogenic iron compounds were able to remove the chromate from the polluted water; however, Zn remained in solution. Encapsulated iron compounds adsorbed chromate and carboxylate groups in alginate were able to adsorb Zn cations (Fig. 2).

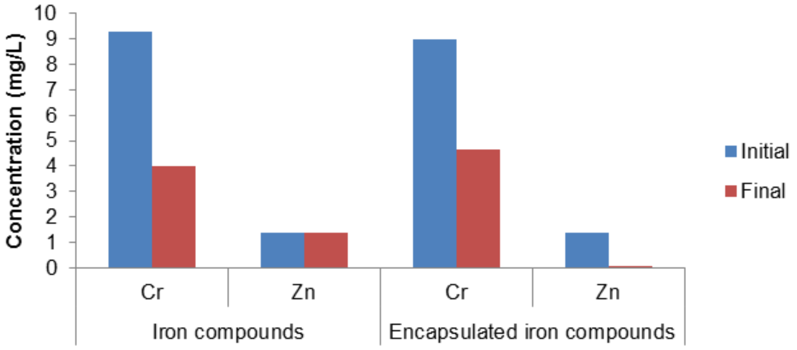

Figure2: Metal uptake of the adsorbents (pH = 4, room temperature).

Consequently, these biogenic compounds offer interesting opportunities for biotechnological applications in water treatment and the implementation in continuous systems.

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OM20

Structural effects on thermodynamics of metal binding with responsive core-shell nanoparticles

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Natural interphases play an important role in the chemical speciation, transport and bioutake of metal ions in freshwaters. Most of the reactive interfaces are soft and water permeable by nature, so that understanding chemodynamics of colloidal-metal complexes necessarily requires a careful examination of the changes in structural properties of soft particle interphase which can occur following variations in the physicochemical medium conditions (pH, ionic strength, temperature or solvent polarity).

In this work,[1] we investigate the impacts of temperature- and salinity-mediated modifications of the shell structure of polymeric ligand nanoparticles on the thermodynamics of divalent metal ions Cd(II)-complexation. The adopted particles consist of a glassy core decorated by a fine-tunable poly(N-isopropylacrylamid) anionic corona.[2,3] According to synthesis, the charges originating from the metal binding carboxylic moieties supported by the corona chains are located preferentially either in the vicinity of the core or at the outer shell periphery (p(MA-N) and p(N-AA) particles, respectively). Stability constants (K_{ML}) of cadmium-nanoparticle complexes are measured under different temperature and salinity conditions using electroanalytical techniques. The obtained K_{ML} is clearly impacted by the location of the carboxylic functional groups within the shell as p(MA-N) leads to stronger nanoparticulate Cd complexes than p(N-AA). The dependence of K_{ML} on solution salinity for p(N-AA) is shown to be consistent with a binding of Cd to peripheral carboxylic groups driven by coulombic interactions (Eigen-Fuoss mechanism for ions-pairing) or with particle electrostatic features operating at the edge of the shell Donnan volume. For p(MA-N) particulate ligands, a scenario where metal binding occurs within the intraparticulate Donnan phase correctly reproduces the experimental findings (Figure 1).

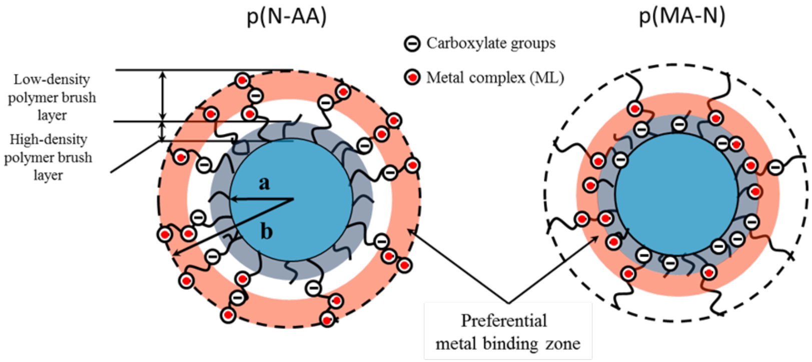

Figure 8: Preferential locations of metal binding in the shell compartments of p(N-AA) and p(MA-N) particulate ligands.

This study provides new insights into thermodynamics of metal binding by responsive core-shell nanoparticles whose reactive sites are heterogeneously distributed in the radial direction from core to outer shell compartment. As such, the study highlights (i) so-far poorly studied relationships between particle electrostatic and temperature-mediated structure heterogeneities, and particle reactivity toward metallic ions and (ii) points out the shortcomings of thermodynamic framework (*e.g.* NICA-Donnan, WHAM, CD-Music models) commonly adopted for quantifying metal binding with colloidal phases.

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OM21

Mechanistic study of the ion binding behaviour of iron oxides and organo-mineral composites

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Nanosize colloidal particles, such as natural organic matter (NOM) and iron (hydr)oxides, control the mobility and bioavailability of trace elements in soil and aquatic systems. Organo-mineral composites formed by the association of iron (hydr)oxides and NOM are widespread in these systems and play an important role as scavengers of bioessential elements and contaminants. In contrast to pure iron (hydr)oxides however, the adsorption behaviour of iron (hydr)oxide organo-mineral composites can significantly differ from their pure mineral and organic components. Macroscopic and microscopic information of the ion binding behaviour in the organo-mineral composites is needed to establish the mechanisms through which contaminants are adsorbed at the solid-solution interface and to develop new remediaton procecures to minimize punctual and diffuse pollution.

In the present study, we investigate copper and arsenate binding to goethite, ferrihydrite and to several organo-mineral composites. The adsorption of both ions was studied as a function of pH and C content, although factors such as the nature of the OM or the presence of major cations were also considered. The results reveal that the presence of organic matter is an important factor capable of enhancing the adsorption of inorganic cationic contaminants, whereas changing the nature of the organic matter present in the organo-mineral composites has little effect on this enhancement. At the same time, increasing the carbon content in the composites produces a decrease on the arsenate binding. These results are attributed to the presence of additional reactive sites at the mineral surface associated with the organic matter, the presence of new high-affinity sites and to an increase of the negative electric potential at the solid-solution interface.

The local structrure of the adsorbed ions was evaluated using EXAFS, determining the molecular binding mechanisms of the end-member mineral and organic phases and organo-mineral composites. This information was used to constrain thermodynamic surface complexation models, specifically BSM and NOM-CD model. For arsenate ions, the NOM-CD model was used in combination with the spectroscopic information to describe the competing effect between arsenate and humic substances for the mineral surface. When the OM present in the organo-mineral composites becomes soluble, the reactive sites associated with the mineral surface are again available to bind arsenate or other oxyanion, which causes a decrease on the arsenate mobility at higher pH values. In the case of copper, the results obtained, in combination with previous works on sorption to bacteria, humic substances and iron (hydr)oxides coated with humics, demonstrate the importance of the carboxylic groups for metal binding and mobility in natural environments. The modelling of the copper adsorption on the composites predicted an additive behaviour when iron (hydr)oxide is the dominant phase in the composites, but when the contribution of OM in the composites increases the copper binding deviates from the additivity.

OM22

Solid-solution partitioning of Rare Earth Elements in mine-tailings and soils in China: experimental results and multi-surface modelling.

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The strongly growing use of Rare Earth Elements (REE) in industry, especially high-tech applications, medicine and agriculture has resulted in their increased emission into the environment during the last decennia. The transport and availability of these elements depends on their solid-solution partitioning and speciation.

Here we study REE solid-solution partitioning in mine tailings and soils from a mining area in Southern China. The experimental results were interpreted with the help of a process-based multi-surface model which has been parameterized in this study for use with REE. To our knowledge no such model is available for REE in soils and sediments. The model is evaluated by comparing modelled with measured REE partitioning in soils.

Several experimental plots were installed on site, amending tailing material with organic matter and planting various plant to study the possibilities of phyto-stabilisation and phyto-extraction. Samples were taken from these plots and from untreated material. Pore water was sampled in some plots with rhizon-samplers. In all soil samples we determined total the metal concentration, the geochemically reactive metal concentration with 0.43 M HNO_3 [1] and contents of organic matter, aluminium- and iron-(hydr)oxides and clays. Soil and sediment samples were extracted with a dilute $CaCl_2$ solution as a proxy for their pore-water composition.

Here we used a multi-surface model implemented in the platform ORCHESTRA with various sub-models for the reactive surfaces including the NICA-Donnan model for metal binding to particulate and dissolved organic matter, the Generalized Two Layer Model (GTLM) of Dzombak and Morel for metal binding to mineral (hydr)oxides and the 2 SPNE model to describe metal binding to clays. Generic model parameters for REE were not available for the NICA-Donnan model and were obtained by fitting to literature data of REE binding experiments with purified humic material in an accompanying study [2]. Based on measured solid phase reactive concentrations of REE and other metals, contents of organic matter and Al/Fe-(hydr)oxides and solution pH and DOC concentration, we predicted dissolved REE concentrations in pore water and $CaCl_2$-extracts and compared the results with measured dissolved concentrations.

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OM23

Reversible sorption kinetics and the adsorption isotherm

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For adsorbates such as dissolved nanoparticles, molecules or ions that undergo no structural changes upon adsorption the kinetics of adsorption of to a planar solid surface can be described in very similar terms. There are always two essential steps: (1) the transport step from bulk solution to the subsurface layer and (2) the attachment-detachment step that is involved in the transfer of the adsorbate from the subsurface to the adsorbed state. The subsurface layer is located at a nanoparticle or molecular distance from the solid surface. The transport step is based on the presence of a diffusion layer. For adsorption from a dilute solution, the characteristic time to saturate the surface is usually long compared to the time needed to establish a steady-state diffusion layer. The thickness of the diffusion layer and hence the transport coefficient depends on the diffusion coefficient *D* and the geometry of the flow field; it is a constant for a given experimental set-up and chosen adsorbate/solvent system. The attachment and detachment step can be based on a Langmuir type approach in which the kinetics are a function of the adsorbate concentration and the surface coverage. In the case of ion adsorption the effect of electrostatic interactions can be considered to be an additional part of the attachment-detachment step. In this case the adsorption kinetics are also a function of the local electrostatic potential. Based on these concepts the rate of ad- or desorption can be described with [1]:

$$\frac{\Gamma_m d\theta}{dt} = \frac{k_t k_{a,\theta}(1-\theta)}{k_{a,\theta}(1-\theta)+k_t}\left(c_b - \frac{k_{d,\theta}\theta}{k_{a,\theta}(1-\theta)}\right) \equiv k_{eff,\theta}\left(c_b - \frac{k_{d,\theta}\theta}{k_{a,\theta}(1-\theta)}\right)$$

where $\Gamma_m d\theta/dt$ is the rate of ad- or desorption, θ the normalized adsorbed amount ($\theta=\Gamma/\Gamma_{\square}$) at time *t*, k_t the transport rate coefficient (depending on the cell geometry and/or flow conditions), $k_{a,\theta}$ and $k_{d,\theta}$ the ad- and desorption rate coefficients that in general may depend on θ, c_b the applied adsorbate concentration, and $k_{eff,\theta}$ the effective rate coefficient that incorporates both the transport and sorption coefficients.

In the equilibrium situation (no net ad- or desorption flux) $\Gamma_m d\theta/dt$ □= 0 and $c_b = c_{eq}(\theta)$ thus

$$\frac{k_{d,\theta}\theta}{k_{a,\theta}(1-\theta)} = c_{eq}(\theta)$$

with $c_{eq}(\theta)$ the equilibrium concentration that corresponds with the adsorbed amount θ at time *t*. Therefore, when the equilibrium isotherm, $\Gamma_m\theta(c_{eq})=\Gamma(c_{eq})$ is know, this information can be used to describe the adsorption ($c_b > c_{eq}$) / desorption ($c_b < c_{eq}$) kinetics:

$$\frac{\Gamma_m d\theta}{dt} = k_{eff,\theta}\{c_b - c_{eq}(\Gamma)\}$$

The difference $\{c_b - c_{eq}(\Gamma)\}$ is the driving force for ad- or desorption. The value of $k_{eff,\theta}$ can be calculated when the rate of ad- or desorption and the equilibrium adsorption isotherm are known. When only the equilibrium isotherm is known already some predictions can be made with respect to the ad/desorption rates.

Specific attention will be given to the kinetics that result for Langmuir and high affinity adsorption isotherms and the model will be illustrated with various experimental results.

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OM24

Interfacial tension of TPM in the presence of nanoparticles of silicon dioxide

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The study of the formation of interfacial adsorption layers consisting of surfactants and nanoparticles is a necessary task for the understanding and controlling the process of obtaining emulsions.

In this work, the interfacial tension was studied to encapsulate the active agents by introducing submicron and nanocontainers into the matrix of the material.

Based on the analysis of literature data, it has been established that, studies of the colloidal-chemical properties of TPM are an important aspect for the controlled synthesis of nanocapsules based on it.

In the work, the interfacial tension measurements of the TPM were measured at various pH of the aqueous phase (pH = 3, pH = 7, pH = 9).

At all the investigated pH values, a significant decrease in surface tension with time is observed, which is evidence of the presence of surfactant in the system and their adsorption at the oil / water interface.

The maximum rate of decrease in interfacial tension was observed at pH 3.

In this regard, it was determined that the most favorable media for the preparation of emulsions is alkaline media, under which the TPM hydrolysis process also takes place, and further polycondensation of the hydrolysis products actively adsorbed on the surface of the hydrophilic particles of silicon dioxide.

OM25

Multi-scale modeling of dynamics in clay/water systems

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Numerous experimental and theoretical studies have focused on predicting the performances of clay minerals as barrier materials in the containment of high-level radioative waste by evaluating the diffusion of mobile species in compacted, water-saturated Na-bentonites. One diffulty arises from the complex, multi-porosity structure of clay materials.

Molecular dynamics simulations, which describe the evolution of matter at the atomic scale, allow to access adsorption properties at the surface of the clay layer. Ions and water molecules show relative different behaviors at the interface. In any case, the presence of the clay surface induces a slowing down of the mobile species, with diffusion mechanisms different from bulk aqueous solutions [1-3], which can be compared with neutron diffusion measurements. If this type of simulations is helpful to understand the water/mineral interactions in detail and interpret experiments at the same scale, it is limited to ideal systems with relatively small dimensions.

However in a multiscale approach, we will show how the values of the results obtained from molecular dynamics simulations can be directly used in Brownian dynamics simulations to simulate the diffusion of tracers (water and ions) through a micrometric clay sample with a complex multiporous structure [4].

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Flocculation of plate-like colloids induced by polyelectrolytes

OM26

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Flocculation is a key process in numerous environmental and industrial technologies, such as purification of waste-water and civil engineering. Its optimization relies on understanding the formation and structure of the aggregates forms. There is a clear need to extend the study of flocculation from spherical colloids to anisotropic particles such as the ubiquitous clay colloids (platelets). We study clay flocculation by ionenes, model cationic polyelectrolytes with a regular charge density, which can be tuned to match/mismatch the clay charge density. We posses extensive knowledge of ionene behaviour in aqueous solutions from small angle neutron scattering and NMR studies [1,2]. Previously, we have also demonstrated the importance of small angle X-ray scattering (SAXS) in the study of clay flocculation by inorganic salts [3].

Combination of turbidity and zeta-potential measurements allowed us to identify the optimal flocculation conditions for ionene-clay mixtures. For all systems studied flocculation started consistently at ratios of positive and negative charge significantly below 1 (as low as 0.3), indicating highly ionene-deficient aggregates [4]. This early onset of flocculation in clay–ionene mixtures is reminiscent of the behaviour of multivalent salts and contrasts with that of monovalent salts, for which a large excess amount of ions is necessary to achieve flocculation [3]. Further, we studied the structure of clay-ionene aggregates by a combination of small angle X-ray scattering (SAXS) and scanning transmission X-ray microscopy (STXM) (see Figure 1). We see a clear evidence for the formation of clay tactoids (regular stacks of clay platelets) within the otherwise loose aggregates. The regular stacking within tactoids is indisputably demonstrated by the presence of a stacking peak in the SAXS spectra (Figure 1 – right). The repeat distance within tactoids depends on the relative charge density of the ionene chains and the clay surface, with weakly charged chains forming a more corrugated layer on the clay surface.

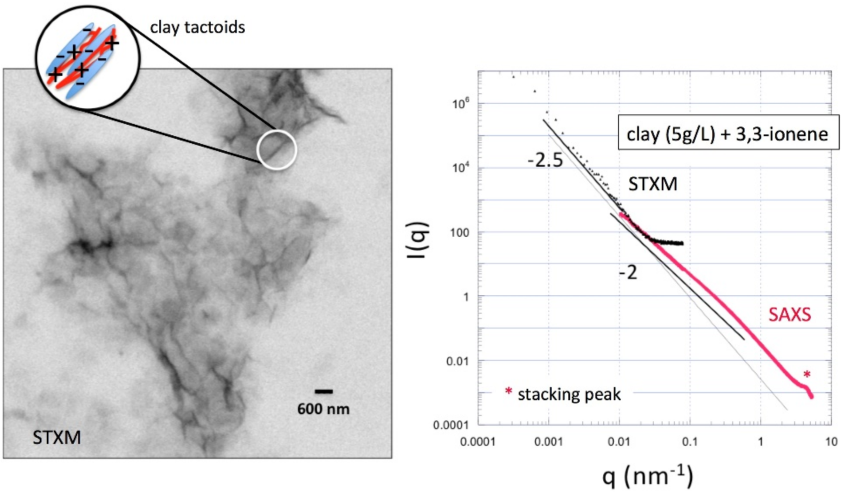

Figure 9: Probing the structure of clay-ionene aggregates, spanning the nm and µm range, by a combination of scanning transmission X-ray microscopy (STXM) and small angle X-ray scattering (SAXS).

STXM images are treated in order to derive a corresponding scattering curve (Figure 1 right) [5]. The overlap with the SAXS curve is good and the resulting combined SAXS+STXM data gives us access to a scattering curve spanning 4 decades in length scale. With such curves we are in the position to assess the multi-scale structure of the aggregates formed: from nm structuring within the clay tactoids to the density and organization of the aggregates on the µm scale.

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OM27

Bio-functionalized MCM-41 silica for heavy metal treatment of water

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The pollution of warer bodies by heavy metals like Cd, Pb, Hg etc. is a menace brought about by rapid industralization. They are extremely toxic to plant and animal health and a prolonged exposure to these elements can cause serious damage to health[1]. This research work is based on the synthesis of mesoporous silica, MCM 41, and utilizing its highly ordered porous nature to graft it with cysteine, an amino acid produced in plant and animal cells which exhibits a high binding affinity to heavy metals [2]. The bio-functionalized MCM silica is then encapsulated into biopolymer beads[3] which are used to fill a column for wastewater purification. The heavy metals can then be recovered for reuse and the beads can then be reused for further purification cycles. Figure 1, depicts a pictoral representation of the wastewater treatment setup that was used.

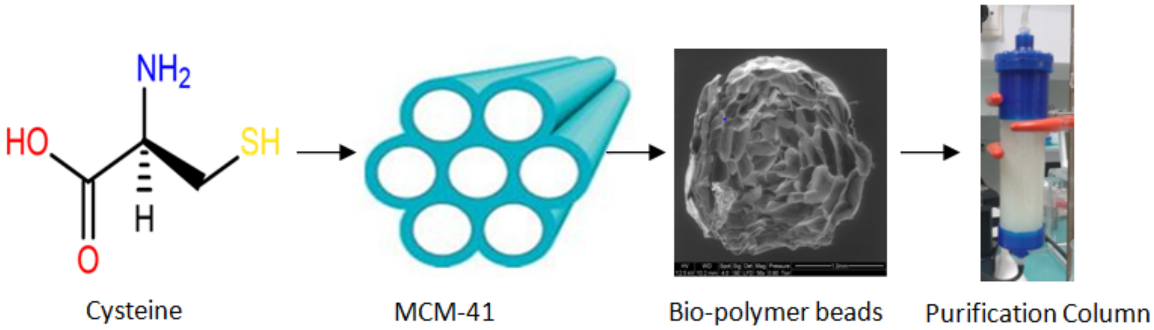

Figure 1: Schematic representation of the proposed wastewater treatment model

The structure of silica along with the porosity is checked by X-ray diffraction and the grafting of cysteine is measured using the CHNS Analyzer. Heavy metal concentration before and after contact with the sorbent material is measured by Inductively Coupled Plasma Spectroscopy (ICPMS). Sorption properties (capacities, kinetics and effect of interfering ions…) are extensively studied in dynamic mode. The beads show a great degree of activity; they efficiently adsorb and desorb heavy metals, thus a novel method that serves two functions i.e.- the purifcation of water and recovery of heavy metals for reuse is proposed. This method runs along the lines of green chemistry and helps environmental remediation.

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OM28

Blue energy by Capmix methods: combination of polyelectrolyte- and membrane-coated electrodes

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Salinity or blue energy sources exist everywhere in nature and they are associated to the mixture of two systems with different compositions. This type of energy generation is inherently renewable and clean, as neither CO_2 nor thermal contamination take place. Remarkable advances in fundamental studies, together with experimental investigations and field demonstrations have been carried out towards finding efficient methods in the past decade [1]. They are based on the variation of the capacitance of the solid/liquid interface when the salinity of the solution in contact is changed, and it has been shown that it is possible to convert the free energy of mixing directly into electric energy. One of the approaches is known as CDP [2] (Capacitive energy extraction based on Donnan Potential) and it consists in implementing one activated carbon electrode in contact with a cationic membrane and the other with an anionic one producing a Donnan voltage difference between both electrodes. Another possibility is the use of the coating of electrodes with a thin polyelectrolyte layer (Soft Electrodes) [3]. Both methods are self-sufficient, since the origin of the voltage difference is the Donnan potential of the membranes and/or the polyelectrolyte coating separating the solution from the carbon particles.

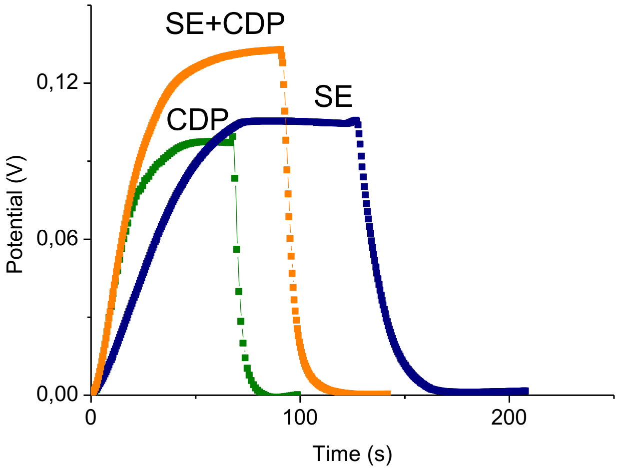

Figure 10: Open circuit voltage in the Capmix cell, when fresh and salt waters are exchanged in membrane- (CDP) and polyelectrolyte- (SE) coated electrodes, and in their combination.

In this presentation we propose a method that successfully uses both principles, combining at the same time the advantages of each of them (Figure 1): a faster kinetics due to the ionic exchange membranes and an increment of the Donnan potential difference arising from the polyelectrolyte coating. Results will be shown regarding the optimum power production with these combined electrodes.

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OM29

Antibiofouling surface modifications using bioactive molecules

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Fouling is the main problem encountered during membrane filtration. It causes a permeability loss, which means a reduction of the productivity. Chemical cleaning is generally used to restore performances of the membrane. Used at high frequencies, the cleaning agents are responsible for a premature membrane ageing caused by the degradation of the polymer material and can lead to water pollution.

The development of antifouling membranes for water treatment would reduce the introduction of cleaning agents in the water cycle. This work focuses especially on biofouling, which refers to a fouling caused by microorganisms. Bacteria used a cell-to-cell communication called *quorum sensing* to form biofilms. This process can be disrupted by using quorum sensing inhibitors in order to prevent biofilm formation. Surface modification via bioinspired approaches combining a biological activity and the modification of physico-chemical properties of the material is recommended to limit biofilm development. In this frame, membrane surface modifications were performed using two approaches, adsorption of Vanillin and grafting of vanillin methacrylate (VMA) as bioactive molecules that would also affect the membrane surface moiety (hydrophilicity) [1, 2]. The aim of this study is to modify commercial polyethersulfone (PES) membrane typically used for water treatment by these two approaches. Then, physico-chemical and antibiofouling properties of the new membrane have been characterized by adhesion test and quantification of biological products.

Vanillin was adsorbed on PES membrane (3M, MicroPES® 1F PH) by soaking in 3 g/L vanillin solution for 3 h. Vanillin methacrylate (VMA) was covalently bonded onto the PES membrane by UV-grafting in a reactor under argon atmosphere (lamp TQ150 Hanau Heraeus, Hg middle pressure). The VMA solution was prepared at the concentration of 50 mmol/L. The time of irradiation used was 5 min. Specific band of vanillin and grafted VMA has been determined by FTIR-ATR (Nexus Thermo Nicolet). Biofilms have been developed on membrane surface placed on agar plate and a 10^6 CFU/mL bacterial suspension (*Pseudomonas aeruginosa* CIP 103467) was dropped on for growth inhibition assays during 24 h at 37°C.

Surface characterization using FTIR mapping highlights the differences between the two surface modification approaches. An effective adsorption of vanillin and grafting of VMA at the membrane surface is observed on FTIR mapping, showing a good homogeneity of the deposit layer. However, the efficiency in terms of adhesion and biofilm development inhibition is limited due to the instability of the molecule at the membrane surface. At the contrary, the grafting approach leads to the covalent binding of the VMA. Impact of the membrane surface modification is observed on the bacterial development as shown in the figure 1. The effect on the biofilm development has to be further investigated and quantified, especially considering the grafting approach.

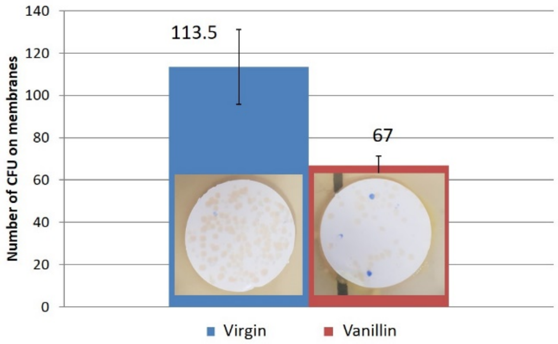

Figure 11: Number of CFU observed on virgin and modified membranes by adsorption of vanillin (n=2) after 24h bacterial growth

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Ensemble of soft electrodes and ionic exchange membranes for capacitive deionization

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There is no need of stressing the social importance of water treatment, particularly desalination, to make it usable for drinking or agricultural purposes. One of the desalination techniques that is currently well established is Capacitive Deionization (CDI), as it is a cost-effective, energy efficient method to remove ions from aqueous solutions. Its basis relies on the fundamentals of the solid-liquid interface science: the ions of the solution in contact with charged porous electrodes migrate towards them, building-up the electrical double layer. The efficiency of the method was improved by using ionic exchange membranes in contact with the electrodes[1,2] due to the ion selectivity of the membranes in the transport from solution to the electrodes. Also, it has been shown[3] that a polyelectrolyte coating (Soft Electrodes) provokes a similar effect, through deposit of the layer on the inner part of macropores. In this work, we use both techniques at the same time by arranging a positive polyelectrolyte-coated electrode in contact with an anion exchange membrane and the opposite for the other electrode (negative polyelectrolyte and cation exchange membrane). The obtained experimental results show an enhancement in the salt adsorption that can be explained by analyzing the theoretical model of the ion transport in this process.

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OM31

Adsorption and magnetic filtration of pollutants by a biochar-based composite

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Biochar, defined as the carbon residue obtained from the thermal decomposition of biomass, can be used for a wide variety of applications, such as soil amendment, adsorption for water and air pollutants, catalysis, electronic industry or hydrogen storage. For the removal of pollutants from water, the association of biochar with magnetic particles inside a composite material enables the sorbent to be easily separated by magnetic filtration from the decontaminated water after the adsorption step [1]. In this work, the chemical and physical properties of a magnetic biochar obtained from a biorefinery residue have been investigated, with the combination of a classical sorption study with a physical study for the understanding and optimization of the magnetic separation.

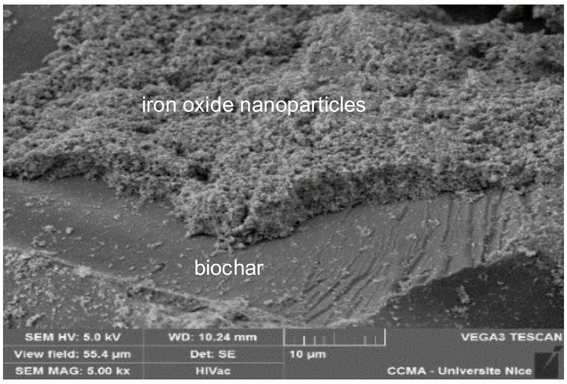

Figure 12: SEM photograph of the biochar-based composite

The magnetic biochar nanocomposite (MBC) was obtained by an *in situ* alkaline coprecipitation on the biochar, at room temperature, of iron (II) sulfate and iron(III) chloride chlorides. The composite was then characterized by granulometry, SEM/EDX, XRD, FT-IR and magnetometry, showing the close association of biochar and the iron oxides nanoparticles. Adsorption experiments were then carried out using methylene blue as model compound for cationic, hydrophilic organic contaminants. The effects of contact time, pH values and dye concentration were investigated, showing a dependence of pH and concentration on the kinetic data, which were well fitted by a first-order model.

Magnetic filtration experiments were performed after an adsorption step by pushing the suspension through a magnetic filter composed by a disordered network of steel wool wires placed between the poles of an electromagnet. The electromagnet magnetizes the steel wool which attracts the magnetic composite and thus separates it from the purified water. The separation efficiency was optimized as a function of the ratio between the hydrodynamic forces (related to the velocity of the fluid flow) and the magnetic forces related to the strength of the applied magnetic field.

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OM32

Dissolved organic sulfur photomineralization in aquatic systems

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Despite its aboundance and its potential effects on climate and metal bioavailability, the biogeochemical cycle of dissolved organic sulfur (DOS) in aquatic systems is still poorly understood. For instance, a significant knowledge gap concerns the DOS mineralization mechanism.[1] Based on recent HRMS studies,[2,3] we hypotesized that photomineralization of DOS to sulfate might represent an important process in sulfur biogeochemistry.

To test this hypothesis, natural waters of different origin were irradiated with UVB light. Sulfate photoproduction was observed in every case, implying that DOS photomineralization is a general process. Model compounds were also tested in order to identify organosulfur compound classes able to produce sulfate upon photooxidation. Based on our laboratory results, we estimated sulfate photoproduction rates in environmentally relevant conditions. Our results showed that sulfate is produced at least 100 to 1000 times faster than any other known DOS photoproducts (COS, CS_2), suggesting that photochemical mineralization likely represents an important driver in the DOS cycle.

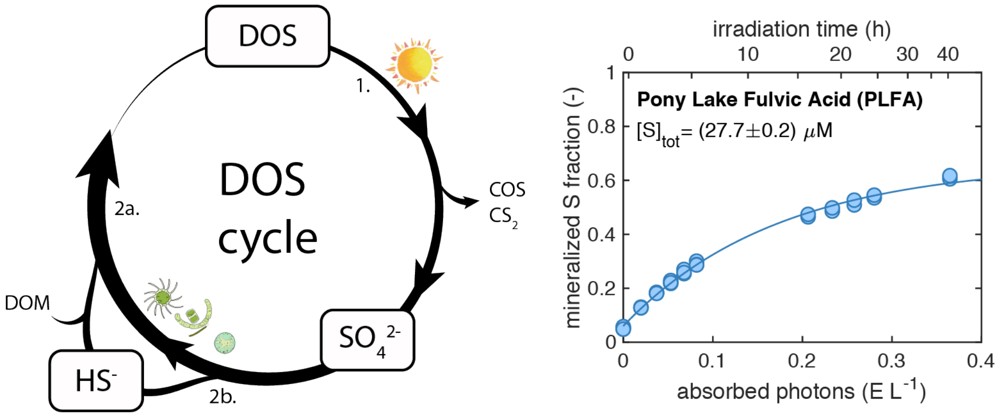

Figure 13: Left – Simplified overview of DOS cycle in water based on our experimental findings: 1. DOS photochemical oxidation; 2a. direct phytoplankton sulfate uptake followed by DOS excretion (sunlit waters); 2b. microbial sulfate reduction followed by abiotic H_2S incorporation in DOM (sediments). Right – Sulfate photoproduction from Pony Lake Fulvic Acid (20 mg_C/L) during UVB irradiation. After 40 h, about 60% of the starting DOS was converted to sulfate.

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PL2

New challenges for the stable isotope analysis of organic contaminant biodegradation

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Enzyme-catalyzed oxygenations are among the most important biodegradation and detoxification reactions of organic pollutants in contaminated soil and water. Because such processes typically take place over timescales of decades and lead to products that are difficult to detect, it is very challenging to quantify the extent of oxidative biodegradation. These issues can be circumvented with compound-specific isotope analysis (CSIA), where the extent of transformation are inferred from changes of stable isotope ratios organic pollutants in the remaining pollutant at natural isotopic abundances and *a priori* knowledge of isotope effects pertinent to enzymatic oxygenations.

However, the kinetics and rate-limiting of such reactions may be governed by enzymatic activation of molecular O_2 which do not involve a transformation of the organic pollutant. Little is known to date about the relative contributions of O_2 activation to the rate of oxidative pollutant removal from a contaminated environment. Our recent work showed that oxygenations by flavin-dependent monooxygenases[3] only lead ot measureable pollutant isotope fractionation in cases where O_2 is bound and activated prior to substrate binding. Conversely, in Rieske non-heme ferrous iron dioxygenases,[1,2] isotope fractionation is modulated by the extent of oxygen uncoupling and formation of reactive oxygen species. These examples illustrate how different catalytic cycles of common oxygenases may determine the applicability of CSIA

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KN5

How does the response of whole-cell metal-sensing bioreporters reflect the dynamics of metal biouptake?

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Despite the growing attention drawn by the environmental science community to whole-cell metal bioreporters in *e.g.* ecotoxicological and monitoring studies, there remains many difficulties to interpret and predict on a quantitative level the response of such biosensors in contact with media containing target metal species. These difficulties mainly originate from the intricate evaluation of the coupling between metal partitioning between extracellular, bio-interfacial and intracellular compartments,[1-3] and the connection thereof with *e.g.* the luminescence produced by the biosensors (Figure 1).

In this presentation, a physicochemical rationale is elaborated for the response of metal-sensing whole-cell bacterial reporters on the basis of a flux-based theory successfully confronted to experimental data. The conceptual framework marks a rupture with the conventional exploitation of bioreporter data, which generally consists in the establishment of calibrated dependence of bioreporter signal intensity on metal concentration in solution and in the subsequent 'reading' of metal content in environmental samples. Instead, the formalism quantitatively explains the dependence of the time derivative of bioreporters signal on bulk concentration of metal ions and on the concentration of bioreporter cells in solution. It further integrates the paramount contributions of cell surface electrostatics and cell metal-binding capacity to biosensor response, both governed by cell surface charge, medium salinity and by the presence of soft surface appendages at the outer cells periphery. For the sake of demonstration, the theoretical framework is here derived for a poorly metal-complexing external solution. The developments lead to expressions of the relevant fluxes pertaining to metal biouptake, to the formation of complexes between internalized metal ions and transcriptional regulators, and to the conversion of activated transcriptional regulators into light. The contributions of these various fluxes to the overall biosensor response is established. Comparison between theoretical predictions and experimental data measured on cadmium-sensitive luminescent *Escherichia coli* bioreporters differing in terms of surface structure composition and surface electrostatics, elegantly supports the bases of the formalism. An important component of the theory is its explicit integration of the possible limitation of the biosensor response by conductive diffusion of metal ions from bulk solution to the metal transporter sites located at the cell membrane. This element enables a critical assessment of the validity of approximate thermodynamic models, *e.g.* the Biotic Ligand Model.

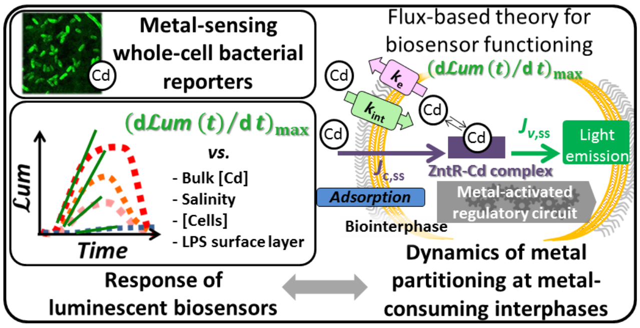

Figure 14: Functioning of luminescent whole-cell bacterial reporters for cadmium detection.

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Screening of fungal isolates collected from soils in the bioremediation of trace metals (Cd, Cu, and Pb)

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Trace metals like cadmium (Cd), copper (Cu), and lead (Pb) are persistent and toxic pollutants[1]. Their natural biogeochemical cycles are disrupted by the anthropogenic emissions because trace metals are accumulated in the environment[2]. They are the second most important pollution in the world, after polycyclic aromatic hydrocarbons (PAH)[3,4]. Innovative approaches in remediation methods are needed[4,5].

Fungi are pioneer and engineer species in the soils. Their mycelium can colonize soils, even highly contaminated. The bioremediation potential of fungi against organic and inorganic pollutants is increasingly studied[6,7].

The aim of our study was to evaluate the biosorption abilities of 28 fungal isolates against Cd, Cu, and Pb in liquid medium. One Zygomycetes, 12 Ascomycetes, and 15 Basidiomycetes have been isolated from contaminated industrial (PAH and/or trace metals) and natural forest soils. An experiment was developed in order to evaluate the fungal tolerance (in agar medium) and the fungal biosorption (in liquid medium)[8]. The pH evolution and the biomass production were also recorded during the experiment.

Tolerance profiles were obtained with each fungal isolate and each metal at different concentrations (from 10 to 1000 mg.L^{-1}). The biosorption profiles were different according to the isolate and the metal. Cd and Pb were globally more absorbed than adsorbed. However, adsorption was higher than absorption for Cu. Several fungal isolates revealed an interesting potential for future mycoremediation studies. For examples, *Absidia cylindrospora* biosorbed 43% of Cd and 65% of Pb ; *Chaetomium atrobrunneum* biosorbed 42 % of Cd, 42 % of Cu, and 65 % of Pb; and *Perenniporia fraxinea* biosorbed 41 % of Cd and 35 % of Cu. *Coprinellus micaceus* was able to biosorb 100 % of Pb.

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OT2

Transport of Oxaliplatin and Carboplatin in natural soil-water environments

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In the last decades, many pharmaceuticals and their derivatives have become recognized as widespread, potential emerging pollutants, and linked to toxicological impacts on ecological systems. Recently, there has been growing concern regarding the occurrence and fate of platinum-based anticancer agents in hospital effluents, surface water and groundwater, as their removal by wastewater treatment processes is limited [1]. Better understanding of transport and fate of these pharmaceuticals in the subsurface could improve predictions of their environmental impact and facilitate the design of remediation efforts.

Here we discuss the transport characteristics of the commonly used anticancer agents oxaliplatin ($C_8H_{12}N_2O_4Pt$) and carboplatin ($C_6H_{12}N_2O_4Pt$), and their derivatives, through packed, saturated sand and soil columns, under controlled and environmentally relevant redox conditions. Oxaliplatin is prone to hydrolysis and ligand exchange as a function of pH and electrolyte activities, and it is therefore a source of both mobile or sorbed Pt complexes in the subsurface [2], while carboplatin exhibits greater stability under different environmental conditions [3].

In sand, oxaliplatin transport was studied as a function of two added natural chelators (citrate and humic acid), whereas in soil, the transport was studied under four continuously monitored, environmentally-relevant redox conditions: oxic, nitrate reducing, iron reducing and methanogenic. In sand, the transport was only slightly retarded; oxaliplatin retention was about 7%, and affected only mildly by added citrate, and by humic acid under buffered pH. Transport with unbuffered humic acid was affected significantly by pH variations, and exhibited strong retention at pH<8. In soil, similar breakthrough patterns of oxaliplatin species were found for all redox conditions, exhibiting stronger retardation than in sand, and nonlinear, reversible retention of about 85%. The strongest retention was observed under iron reducing conditions, whereas the weakest retention was under methanogenic conditions. Increased cation activity in the inlet solution appears to promote weaker sorption. Overall, none of the chelators or soil redox conditions induce a sufficient, long term retardation mechanism for oxaliplatin and oxaliplatin-related species.
Carboplatin transport was studied in sand under oxic conditions, and in soil under oxic and methanogenic conditions. While the retardation factors are practicaly the same as in the oxaliplatin case, the retention in both sand and soil is similar and very low: 4-2%. Carboplatin affinity to both sand and soil surfaces is close to zero. Transport characteristics are very similar under oxic and methanogenic conditions, however modeling results indicate that the transport is governed by different mechanism in each case.

The study indicates that soil composition and pharmaceutical molecular structure are the leading factors affecting oxaliplatin and carboplatin species mobility and fate in the soil-water environment, followed by the weaker factors of redox conditions and cation activities. Moreover, natural soil-water environments seem to be lacking robust retardation mechanisms for oxaliplatin and carboplatin species, and efforts to attenuate their transport in soil-water environments by manipulation of redox or pH regimes will not be sufficient to prevent aquifer system contamination; prevention, reduction, or control of contamination by oxaliplatin and its derivatives may be better achieved by collection and treatment of hospital effluents at source, before they are released to aquifer and soil-water environments. Finally, the results show that similarly structured pharmaceuticals, pertaining to the same pharmocologic class, may exhibit very different behavior and transport characteristics in natural soil-water environments, and should be studied individually.

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Assessment of zooplankton for domestic wastewater treatment

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Whereas wastewater treatment is fully implemented in urban areas, rural communities still encounter difficulties in finding appropriate technologies, given the high installation and operational costs that are typically involved. The search for mild, economical and easy-to-operate systems could find a solution by exploitating living organisms that are able to perform natural decontamination: an interesting example of such an organism is *D. magna*, which is a planktonic crustacean (Cladocera order) that is widely used in toxicity tests. However, it could also be exploited for wastewater treatment purposes given that it is a filter feed organism whose diet is based on ingesting algae and other organic detritus, including protists and bacteria (Gliwicz., 2008). Previous studies have shown the usage of *D. magna* allows reducing the suspended solid content (Pau et al., 2013) as well as the bacterial load (Serra et al., 2014). Thus, *D. magna* allows disinfection and solid content removal through a natural-based wastewater treatment process. However, such a system could also be applied in nutrient polishing. This study aims to combine the filtration capacity of zooplankton with the capacity of natural grown bacterial/algal biofilms in a *D. magna*-containing reactor to reduce nutrient concentrations. Two kinds of experiments were performed: i) Carbon, nitrogen and phosphorus inhibition tests, and ii) Carbon, nitrogen and phosphorus biological removal at different hydraulic retention times (HRTs) in the *D. magna* reactor.

In the inhibition tests, it was observed that the filtration efficiency of *D. magna* decreased by more than 40% from its maximum when COD, ammonium, nitrite and phosphate concentrations were higher than 160 $\mathrm{mgCOD \cdot L^{-1}}$, 40 $\mathrm{mgN\text{-}NH_4^+ \cdot L^{-1}}$, 5 $\mathrm{mgN\text{-}NO_2^- \cdot L^{-1}}$ or 30 $\mathrm{mg\ P\text{-}PO_4^{3-} \cdot L^{-1}}$, respectively. While no significant inhibition was detected for nitrate. Therefore, inhibition tests suggested that *D. magna* could be harmed when they are exposed to primary wastewater. However, they perform well in terms of filtration capacity for treating secondary wastewater. Given this, biologic nutrient removal at continuous flow mode was tested in a *D. magna* reactor by using synthetic secondary wastewater. A significant removal of COD (89%) and total nitrogen (55%) was observed at the highest HRT (3.7 days), but with low phosphate treatment (12%). Decreasing the HRT to 1.1 days resulted in a slight decrease (9%) in the removal of COD, but nitrogen removal decreased to 18%. The nutrient removal kept on decreasing at HRTs <1.1 days. Hence, coupling *D. magna* with bacterial/algal biofilm in a single reactor is shown to be able to polish the organic matter and nitrogen content of secondary wastewater requiring HRTs >1.1 day (ideally 2-4 days).

Wastewater treatment based on the usage of zooplankton (such as *D. magna*) together with bacterial/algal biofilm in a single reactor is an interesting alternative to conventional treatments especially in isolated and low income communities due to its economical operation and installation costs, easy-operation and sustainability. The results presented here indicate that the coupling of *D. magna* filtration capacity together with those of natural grown bacterial/algal biofilms allows a significant reduction in nutrient concentrations in wastewaters when the system is operating at HRTs of > 1.1 day (preferably of between 2-4 days). However, a primary/secondary treatment should be made as high concentrations of nutrients can inhibit *D. magna* activity. In combination with other natural treatments, *D. magna* could provide a solution for wastewater treatment in low income and isolated communities, even permitting water reuse if operated correctly.

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OT4

Transport of organic molecules in environment: insights from retardation in sedimentary rocks

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Organic molecules are widely studied in environmental sciences, marine chemistry, soil- and geo-sciences. Among them, anthropogenic organic matter (AOM) can be potentially released from hazardous waste and migrate through geological rock formation or soils. AOM refers to a wide range of compounds, including both ionic and neutral molecules, polar and apolar molecules. The ionic polar molecules are highly soluble in water and more mobile in soils and rocks. The neutral (poly)aromatic compounds are less soluble, often absorbed by Natural Organic Matter (NOM), but also more resistant against (bio)degradation. For all these compounds, adsorption or absorption processes can slow down their migration in environmental conditions. Consequently, understanding retardation phenomena of soluble organic matter in rocks and soils is crucial for safety assessments of waste disposal, decontamination processes, ore extraction and remediation of soils.

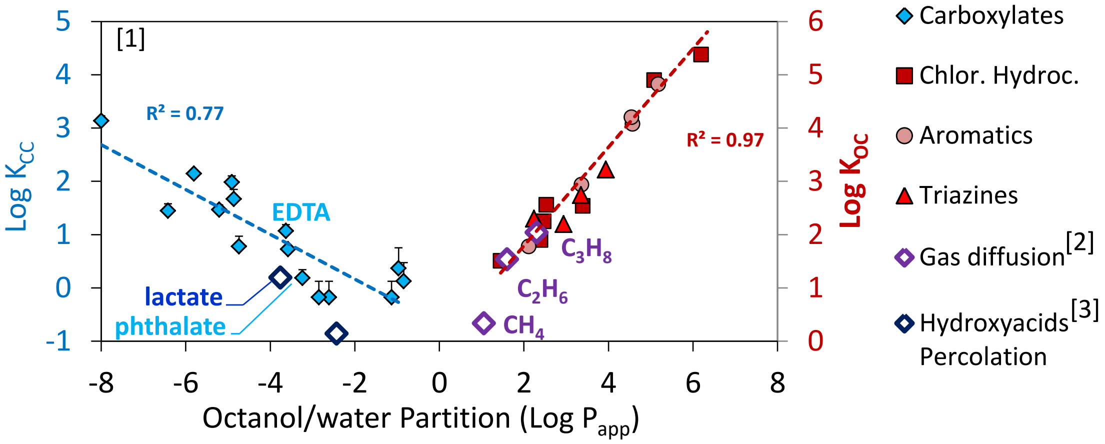

Figure 15: Correlation between octanol/water partition coefficient and adsorption of organic molecules. Adsorption data are normalized by NOM content (OC~0.6%) or clay content (CC~30%).

A considerable effort has been made for 20 years to study migration phenomena in clay-rich geological barriers in the context of radioactive waste disposal. Recent studies emphazised the adsorption of organic molecules on clayrocks[1]. One of our main findings is the correlation between adsorption and hydrophilicity of adsorbates, which highlights the role of various minerals as main sorbing phases (Figure 1). Hydrophobic molecules (red dots, log(P_{APP})>1) are absorbed by natural organic matter, whereas hydrophilic anions (blue dots, log(P_{APP})<-1) are mainly adsorbed on oxides or clay minerals. These sorption data are strengthened by various migration experiments, e.g. *in-situ* diffusion of dissolved gas[2], or percolation of hydroxyacids in compacted clays[3]. One of the main remaining issue is the discrepancy between adsorption data measured by batch experiments and retardation factors measured by migration experiments on highly compacted rocks[4] (Fig. 1, left part in blue) Potential origins of these discrepancies, such as the "anionic exclusion" effect, will be discussed. The outcomes will be also discussed on a more general level, dealing with industrial processes and fate of organic molecules in the environment.

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As removal in Mn-contain groundwater matrices

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Arsenic (As) occurs naturally in some groundwaters, which serve as the main source of drinking water for many people worldwide, especially in South-East of Asia (Bengladesh, India, etc.). Because of this large-scale contamination and the high toxicity and carconegicity of As, it is responsible for millions of deaths around the world. Therefore, strategies to remove As from water using efficient and cheap treatement system are critically needed. Iron(0) electrocoagulation (EC) has gained attention as a low-cost method for As removal from groundwater because it has short supply chain and low energy requirements (small solar panels or car battery provide sufficient power) and, importantly, is easy to operate. In EC, a current is passed through an Fe(0) electrode, such that Fe(0) is oxidized to Fe(II). The production of Fe(II) generates reactive oxidants that readily oxidize As(III) to form As(V) – a less dangerous form of As, and Fe(II) to Fe(III), which forms nanoscale iron precipitates that remove arsenic from solution [1, 2]. However, the type of reactions that occur, and arsenic removal efficiency, depend strongly on the chemical composition of the groundwater. Thus, successful implementation of EC requires systematic chemical and mineralogical studies under varying operating conditions and groundwater chemistry.

In some waters, As and Mn co-occur at high concentrations [3]. Recent work shows that Mn(II) can also be removed from water using an EC system through the oxidation of Mn(II) to Mn(III) and its incorporation into Fe oxides. Moreover different oxidants are responsible of the oxidation of Fe and Mn at different pH and the greatest Mn removal occurs at pH 8.5[4]. Combined, these studies suggest that As and Mn compete for the same pool of oxidants in an EC system and therefore that the efficiency of As removal may be influenced by the presence of Mn. The main goal of this work is thus to understand the extent to which As and Mn are removed during EC when aqueous As(III) and Mn(II) are initially present in the groundwater. In addition, knowledge of the speciation of As and Mn in the solid phase is needed in order to understand the mechanism of contaminant removal (oxidation and sorption) at the different conditions (concentrations of Mn, pH, oxidants).

In this study, experiments were conducted using 10 µM As(III) and either 100 or 1000 µM Mn(II) at pH values ranging from 4.5 to 8.5. We investigated the role of the oxidants on As and Mn removal by running the EC system open to the atmosphere (presence of O_2) or by providing a spike of H_2O_2 (250 µM). Because of the slow kinetics of iron oxidation in the presence of O_2 at acidic pH values, only pH 7.5 and 8.5 were studied in the presence of O_2. All the experiments were conducted in triplicate and speciation of the aqueous and solid phase followed over time for 32 minutes.

Results showed that even in the presence of high concentrations of Mn in solution, As concentrations were less than the 10 µg L^{-1} (WHO limit) in the presence of H_2O_2 after 30 min at all pH conditions. In the O_2 system, As concentrations decreased over time, but did not attain the 10 µg L^{-1} target. Solution pH and the initial oxidant (O_2 vs. H_2O_2) influenced significantly the extent of As and Mn removal. The speciation of As and Mn in the solid phase, as determined by X-ray absorption spectroscopy (Stanford Synchrotron Radiation Lightsource, BL 4-1), showed greater As oxidation at pH 4.5 than at pH 8.5 and at high concentrations of Mn. On the contrary, greater Mn oxidation was observed at pH 8.5 than at pH 4.5. Moreover, in the O_2 system, Mn and As were mainly present in reduced form in the solid phase. These results indicate that the kinetics of As and Mn oxidation and mechanism of removal to the solid phase vary strongly according to type of oxidant present in the system (e.g., $\cdot$OH and Fe(IV), respectively).

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OT6

Biodegradation of aliphatic polyesters in soils: using stable carbon isotope labeling to track polyester-derived carbon

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Over the last few decades there has been a strong increase in the use of plastics in agriculture to increase crop yields, a practice coined 'plasticulture'. One major application area are polymeric mulch films that are used to cover agricultural soils to retain soil moisture, increase soil temperature, and control weed growth. These films are commonly composed of polyethylene, a non-degradable, persistent polymeric material. If not properly collected from the soils after their use, these non-degradable films accumulate in the agricultural soils, thereby negatively impacting soil fertility and subsequent crop yields. One strategy to overcome this problem is to replace non-degradable with biodegradable polymer materials, including aliphatic polyesters. When left on/in the soils after use, biodegradable mulch films are utilized by soil microorganism and thereby converted to carbon dioxide (CO_2), microbial biomass, and water. Yet, the rates and extents at which these polyesters biodegrade in soils remain poorly studied, mainly due to a lack of analytical approaches to track polyester carbon during biodegradation in soils.

This work introduces a novel analytical workflow that utilizes ^{13}C-labeled polyesters to follow their biodegradation in soils. We incubated ^{13}C-labeled polyesters in soils within flow-through chambers coupled to analysis of the effluent gas by isotope-sensitive cavity ring down spectroscopy, allowing us to continuously monitor mineralization of these polyester to $^{13}CO_2$. Additionally, after terminating the incubations, the use of ^{13}C-labeled polyesters allowed us to quantify the polyester-derived carbon that had remained in the soil at the end of the incubations by analyzing the $^{13}CO_2$ formed from combusting small soil aliquots.

We validated this approach and highlight its unique capabilities by tracking carbon of three position-specifically ^{13}C-labeled poly(butylene succinate) (PBS) variants incubated in agricultural soils. Over 425 days of incubation, 65 ± 1 % of the ^{13}C added in PBS was mineralized to $^{13}CO_2$. The rates and extents of mineralization were identical for the three tested variants and thus independent of which carbon position in the PBS was ^{13}C-labeled. Soil combustion showed that 34 ± 2 % of the added ^{13}C-PBS had remained in the soil, thereby demonstrating closed ^{13}C-PBS mass balances over the long incubation period. Using Soxhlet extraction, we showed that most of the ^{13}C that remained in the soil was still present as bulk PBS. Fitting of the data with a biodegradation model showed that (enzymatic) hydrolysis of ester bonds in the bulk PBS polymer was the rate-determining step in overall biodegradation. Furthermore, the modeling results were consistent with PBS biodegradation slowing down when nutrient availability decreased in the soils.

We will discuss both the methodological advancements presented herein and the results from the PBS soil incubation experiments in the broader context of polymer biodegradation in the environment.

Probing ternary surface complexes by in situ infrared spectroscopy

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Attenuated Total Reflection-Infrared spectroscopy (ATR-IR) is amongst the most developped spectral techniques during the two last decades to study the solid/solution interfaces. Its efficiency in determining the speciation of adsorbed ions has been proved in numerous works using different metallic oxides [1]. Its advantage is to probe the system in presence of solution, avoiding the modification of the structure consequently to the dehydration. Some possibilities of ATR-IR remains underexploited, for example its ability to characterize ternary surface complexes defined as *a mineral surface / a bridging species / a second adsorbed species* system.

This type of systems is strongly relevant in the understanding of the sorption of toxic cations onto metal (hydr)oxides in environment. Indeed, the impact of the presence of organic molecules acting as ligands can be crucial, by allowing the uptake of cations in chemical conditions where it is usually not sorbed, or, on the contrary, by keeping the cation in solution due to a strong complexation. Thus, these systems are complex, and obtaining spectroscopic data is an efficient approach to be able to detail the mechanism of the reactions at the solid/solution interface.

We have performed experiments on several metal oxide / ligand / cations ternary systems, for different applications, and the results illustrate both the experimental approaches and the data which could be obtained using ATR-IR spectroscopy. Thus, the effet of citrate ions on the sorption of Co^{2+} on γ-alumina has been investigated by several complementary techniques (ATR-IR, Visible spectroscopy, XPS), and a weak interaction between adsobed Co^{2+} and citrate has been identfiied, leading nevertheless to an increase of the the surface density of cobalt [2]. The limit of the spectroscopic approach on this first system is that the cation is not probed by infrared spectroscopy. On the contrary, the sorption of urnayl ions onto silica in presence of carboxylate ligands is another example where this limitation is not present. Indeed, our experiments have allowed to follow the formation fo ternary surface complexes, by recording simultaneously the in situ spectra of uranyl ions and carboxylate ligands [3].

In conclusion, these studies demonstrate the complexity of sorption mechanism of metals in presence of organic ligands, and how in situ infrared spectroscopy brings molecular-scale information to help to tackle this problem.

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OT7

Investigation of retention mechanisms of dye by lamellar materials through vibrational spectroscopy

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Some countries with rich textile industries are nowadays facing water quality issues as a consequence of impacting dye pollution. In addition to their inherent toxicity, dyes induce modification in water acidity or salinity which has harmful consequences on the photosynthesis of aquatic plants. As dye are hardly biodegradable, water treatment is necessary to get ride of them [1], and adsorption treatment appears as a good candidate with efficient low-cost adsorbents, such as clays [2].

As a matter of fact, lamellar materials are widely used for sorbtion of ions and molecules harmful for health and environment. In order to gain in efficiency in the use of such materials, it is essential to get a deeper understanding of the retention mechanisms at the interface solid/liquid. In this work, anionic clays, namely layered double hydroxides (LDH) have been chosen as model compounds in order to study sorption mechanism. The presence of charged layer induce strong anionic exchange capacity in these materials, moreover their composition and structural parameters are easily controled through mastered synthesis process [3]. This study work has been focused on the the mechanisms that can lead to the capture of polluting molecules. Several model dyes have been chosen (MethylOrange - MO, Carmen Indigo - CI et Orange G - OG) for their charge, symmetry and hydrophobicity. Parameters such as the solution concentration and the activity of the solvant, playing with the nature of ions, have also been explored.

The work presented here rely on vibrational spectroscopies (Infrared and Raman spectroscopies) sensitive to the intermolecular interaction of the dye with its environment particularly at the interface solid/dye. In parallel, X-Ray Diffraction probes the structural modification in the clay during sorption.The experimental results interpreted though the help of simulations (Monte-Carlo, DFT), lead a fine description of ions sorption at the interfaces with these models lamellar materials.

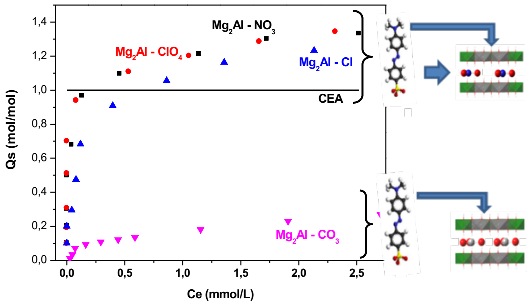

Figure 1: Sorption isotherms of MethylOrange on LDH of various compositions.

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OT8

Surface species of phosphate on goethite. Distribution as a function of pH and surface coverage

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The adsorption of phosphate at the metal oxide-water interface has been intensely studied due to its profound environmental implications. The system phosphate-goethite is normally used as a model system, with abundant information regarding phosphate adsorption-desorption processes. In spite of these facts, there is still discussion on whether the main inner-sphere surface complexes that phosphate forms on goethite are monodentate or bidentate. This controversy can be solved with the aid of InfraRed Surface Titrations (IRST) combined with calculations using the CD-MUSIC surface complexation model. IRST, similarly to what was previously presented by Loring et al. [1] for studying arsenate speciation, is an acid-base potentiometric titration in an infrared cell which directly detects the protonation-deprotonation reactions of phosphate surface species. As it can be exemplified in Fig. 1 for a goethite sample with a total surface concentration of phosphate of 2±0.2 μmol m^{-2}, changing the pH produces very significant changes in the ATR-FTIR spectrum of adsorbed phosphate. Two different surface species could be detected: one species being the result of the protonation of the other species. Thus, IRST enabled to construct distribution curves of surface species as a function of pH at different surface coverages.

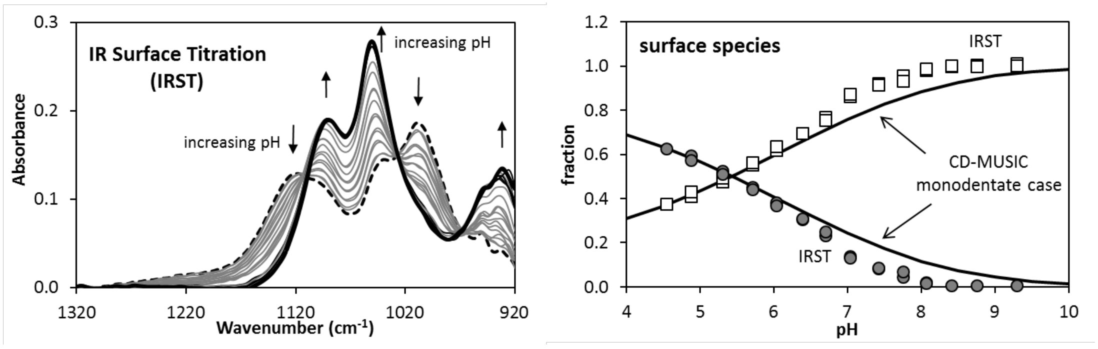

Figure 16: ATR-FTIR spectra (left) of phosphate species at the surface of goethite during a titration run between pH 4.5 and 9.5, and surface species distribution (right) as obtained from the spectra and CD-MUSIC calculations for the monodentate case. Open squares: species before protonation; circles: after protonation. Surface concentration of phosphate: 2±0.2 μmol m^{-2}.

Very accurate distribution curves were obtained for surface coverages of 0.7, 0.9, 1.4 and 2.0 μmol m^{-2}. Surface speciation calculated with the CD-MUSIC model [2] led to very good predictions assuming that both surface species were monodentate, and to very bad predictions assuming the presence of bidentate species. Therefore, the combination of experiment and theory allowed to conclude that monodentate inner-sphere complexes of phosphate prevail at the surface of goethite. The importance of IRST for studying surface reactions of many different IR active substances (humic and fulvic acids, adsorbed pesticides, etc.) will be also discussed.

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OT9

Nanoparticle (NP) interactions with (bio)surfaces probed by single-NP force spectroscopy

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Adversed effects caused by nanoparticles (NPs) on (micro)organisms depend partly on the type and the magnitude of the interactions that control their attachment to biosurfaces. Recognizing that NPs bioadhesion triggers a chain of biochemical processes that potentially disrupt organisms' physiology and lead to toxicity, it seems mandatory to evaluate the propensity of NPs to bind to surfaces of living cells. Currently, NPs ecotoxicological risks are addressed from considerations of the physicochemical surface properties of NPs and cells obtained independently from *e.g.* titration or electrokinetic measurements. The latter necessarily provide an information that is averaged over the whole particle dispersion and cell population, with little direct insight into the relevant interaction processes taking place at *the cell/NP pair level*. Recently, atomic force microscopy (AFM) and the related developments of force nanoscopy have allowed the assessment of bio-nano interactions down to the molecular scale.

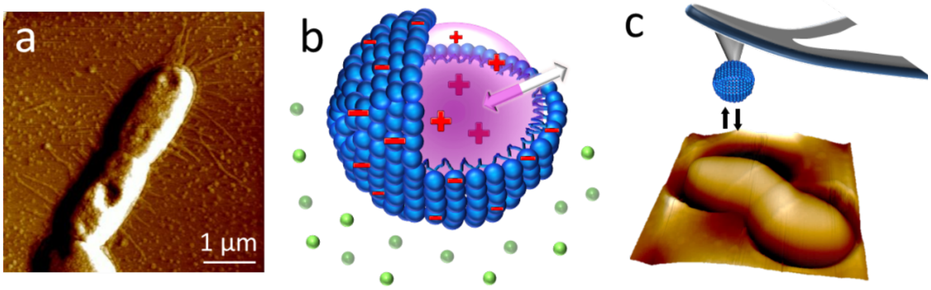

Figure 17: Probing NP-living bacteria interactions.
(a) AFM image of an Escherichia coli decorated by pili. (b) Schematics of a zwitterionic nanodendrimer composed of a positively-charged amine core and a negatively-charged carboxylic peripheral shell. (c) Schematics of the AFM set-up adopted to probe the interactions between a single-NP attached to the AFM tip and a bacterial surface.

In this presentation, we shall discuss how these recent developments of AFM functionalities now make possible the measurement and interpretation of the complex interactions between a single nanoparticle (with diameter below 10 nm) and the surface of a living microbe. For the sake of illustration, AFM-derived parameters pertaining to the adhesion of NPs (*e.g.* fullerenes, dendrimers) to cells envelopes will be discussed in relation with their respective physicochemical surface properties. The latter include not only the NP electrostatic surface features but also the spatial organization of the NP charges, as well as the presence/absence of biomolecules (*e.g.* pili or polysaccharides) decorating the microorganisms periphery. It is anticipated that the methods presented here will be useful to control NPs binding to living organisms upon proper modification of their nano-interphase features.

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- S. El-Kirat-Chatel from the LCPME, CNRS-Université de Lorraine, Nancy, France.

OT10

Role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study

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Aluminosilicates materials are widely used in industry for various applications such as catalysis or zeolites which are currently involved in many depolution processes. More recently in civil engineering with the development of geopolymers, they are used as “sealing layers” in order to avoid the inflow of groundwater in construction pits or for the reinforcement of sand based ground. It has been proved that the nature and the concentration of the alkali cation drive the final properties of the gel [1]. The final properties of these aluminosilicates materials strongly depend on the chemical composition of the alkali silicate solution often used as precursors. The complex physico-chemical properties of silicate oligomers were already studied by NMR [2] and mass spectrometry [3] but there are still open questions.

We developed theoretical tools to characterize concentrated alkali solutions of silicates to understand the structural and dynamical properties of such fluids. Here, the influence of the MOH concentration (M^+ being an alkali cation), as well as the nature of the alkali cation has been investigated by means of classical molecular dynamics using explicit polarization. To this end, polarizable force fields for describing the solvation properties of the hydroxide anion and the silicate oligomers have been developed from non-polarizable force field [4,5].

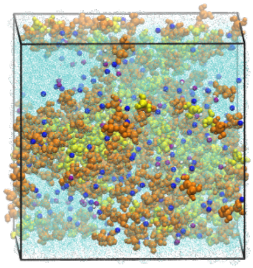

Figure 18: Simulation box of monomers $Si(OH)_4$ (yellow) and dimers $Si_2O_2(OH)_5^-$ (orange) at 2.0 mol kg^{-1} in aqueous solutions of 5 mol L^{-1} of NaOH. For clarity, only Na^+ (blue) and OH^- (purple) close to silicate oligomers are represented (distance ions-Si atoms less than 6 Å).

Simulations of hydroxide alkali solutions from 0.5 up to 9.7 mol L^{-1} have been carried out and structural properties have been calculated. The density, and the WAXS spectra have been calculated and directly compared to the experimental results. A good agreement is observed between the theoretical results and the experiments [6]. In addition, we investigated the effect of the addition of silicate oligomers on the structural properties. Changes in the oligomerization process such as the insertion of alkali inside aggregates and network of silicates oligomer are observed as a function of the nature and the concentration of the oligomers i.e., monomers ($Si(OH)_4$, and $SiO(OH)_3^-$), and dimers ($Si_2O_2(OH)_5^-$, $Si_2O_3(OH)_4^{2-}$).

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OT11

Quinone interactions with iron bearing clays and oxides

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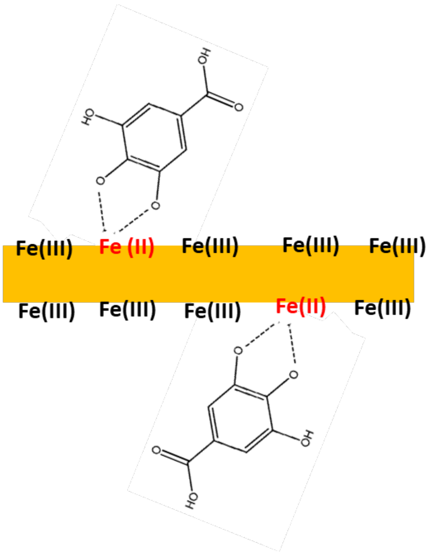
The occurance of organic matter significantly effects pollutant fate in soils and aquifers and also impacts efficiency of soil and water treatment processes. In that respect, a fundemental study was performed on the interactions between quinone molecules (a prevalent moiety in dissolved and solid organic matter) and iron bearing clays and oxide colloids. Galic acid (GA) was chosen as a model quinone because of it's stability and natural occurance in soils and sediments. GA interactions were studied with hematite, magnetite and an amorphous iron-oxide deposited on montmorillonite clay (Fe-MMT). Adsorption experiments revealed an increased affinity to the MMT-Fe over the other two iron-oxides. The adsorption of GA to hematite and magnetite was pH and ionic strength dependant pointing to an outer-sphere electrostatic adsorption mechanism. In contrast, the adsorption of GA to MMT-Fe was independent of pH and salinity indicating a stronger inner-sphere complexation mechanism. This Fe-MMT-GA complex was further characterized by XRD, FTIR and XPS. The results showed further transformation reactions such as redox and polymerization of the GA and reduction of the structural iron. In addition, the resulting complex had increased adsorptive, catalytic and conductive properties. These interesting interactions can occur in soils and sediments under ambient conditions and can in turn significantly effect pollutant sequestration and transformation. Consequently, the findings are relevant not only interms of predicting the fate of pollutants in the environment, but also for the evaluation of in-situ soil and sediment treatment processes such as in-situ chemical oxidation and reduction.



Hypothesized iron (III) reduction and inner-sphere adsorption of GA on Fe-MMT

OT12

Interactions between charged macroions mediated by nanoparticles with spatially distributed charges

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.Interactions between charged macroions in aqueous solutions are of fundamental importance in many technological and biological systems [1,2]. In this work, I will consider an aqueous solution that contains a mixture of spherical nanoparticles and small mobile salt ions, sandwiched between two like-charged planar surfaces [3,4,5]. A mean-filed approach will be improved by considering structural details of the nanoparticles like the excluded volume effect and the charge distributions on individual nanoparticles [2,3,4]. The charge on the nanoparticles is continuously or discretely distributed. The results for nanoparticles with charge distributed on the surface are contrasted with nanoparticles that have all their charges relocated at the center. I will show that the theory predicts a saturation of large nanoparticles close to the highly-charged surface. In the case of asymmetric charge distribution, the orientational ordering of nanoparticles at charged surfaces is observed. The model predicts that the large and highly charged nanoparticles with the charge located on the surface can mediate attractive interactions between like-charged macroions. The conditions for the possible attraction between like-charged macroions induced by nanoparticles will be discussed.

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PL3

From searching for friendly mining technologies to studies on the chemical fate of nanoparticles in terrestrial plants: How gold mining changed my life

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My entire life has been linked to gold mining. Growing up in a mining district allowed me to observe the environmental effects of the mining industry. These experiences drove my life into the world of environmental/chemical engineering and of chemistry. As an environmental scientist/engineer, I dedicated my knowledge to find the way to study the response of plants to heavy metal stress. This led my research group into phytoremediation, one of the most promising plant-based approaches to restore contaminated soils. My research group obtained significant results in the remediation of mine tailings using desert plants such as *Baccharis sarothroides*, *Prosopis* spp., and *Chilopsis linearis*. The extensive work of my research group at the University of Texas El Paso (UTEP) in the field phytoremediation led us to discover that plants could form gold nanoparticles (NPs) from the absorbed gold compounds, for the first time [1]. This discovery allowed us to be part of the UC Center for the Environmental Implications of Nanotechnology (UC CEIN), where we have been studying, for nine years, the effects of metal NPs (nano-CeO_2, nano-TiO_2, nano-ZnO, and nano-CuO) on terrestrial plants, specifically crop plants. Different plant species have been exposed to NPs at varying concentrations in soilless and soil media. Synchrotron-based techniques including X-ray absorption near edge structure (XANES), micro-X-ray fluorescence (μ-XRF), and transmission X-ray microscopy (TXM) have been used to study the biotransformation of NPs. Another primacy of my research group was the discovery, by using XANES, that nano-CeO_2 were taken up and stored, with little or no transformation, in roots of soybean (*Glycine max*), while nano-ZnO was not detected in seedlings' roots [2]. Tissue analysis with μ-XRF, combined with micro XANES (μ-XANES) showed that cucumber (*Cucumis sativus*) plants absorb nano-TiO_2 through the roots and translocate them into the fruit [3]. μ-XANES analyses have also shown differences in the biotransformation of weathered and unweathered nano-CuO in lettuce (*Lactuca sativa*). While weathered particles were almost completely transformed from CuO to Cu (I)-sulfur and oxide complexes, roots exposed to unweathered particles showed Cu as CuO [4]. These studies have shown different levels of biotransformation of metal oxide NPs in plants. In addition, we have found that some of them, including nano-TiO_2 and nano-CeO_2, can be stored in fruits and seeds, while others, like nano-ZnO, have been observed only in roots.

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AGNES: a tool for studying the thermodynamic and kinetic behaviour of nanoparticles

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The electroanalytical technique AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has been designed and implemented for the measurement of free metal ion concentrations in solution [1, 2]. Free concentrations of Zn, Cd, Pb and In [3] have been determined in a variety of matrices ranging from river water to wine or soil extracts. As AGNES can be applied to dispersions without any previous separation of the solid or colloidal phases [4], it is suitable for providing relevant information about the behaviour of nanoparticles, avoiding usual artefacts which may trouble other analytical techniques. Very relevant kinetic and thermodynamic information on the dissolution of ZnO nanoparticles in background electrolyte [5] or in a growth medium [6] was gained with AGNES. For instance, based on Ostwald-Freundlich expression and the obtained data, one can predict the solubility of ZnO nanoparticles for a given nanoparticle radius and a given pH. Work about the dissolution of ZnO nanoparticles in synthetic saliva reveals, once more, the need of taking into account transformations of the NP with a very complex medium (containing phosphates and carbonates). The study of dispersions of In_2O_3 nanoparticles in background electrolyte and in synthetic seawater confirms a marked reduced solubility when compared to bulk $In(OH)_3$.

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OW1

Tuning the hydrophilic-hydrophobic balance of Prussian Blue analogues for the removal of toxic gases in humid atmosphere

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The inclusion compounds in general, particularly Prussian blue analogues, have been a subject of many theoretical and experimental studies as a result of their fundamental significance in understanding the nature of interactions between the molecular/ionic species, and also their practical importance. [1][2] Amongst the various possible technological applications for Prussian blue analogues, the separation of organic compounds appears as very promising. This is because of the chemical properties of these new sorbents which are adjustable. It is indeed possible to design the appropriate ligand and the metal centres for the application targeted. However, the presence of water vapor is always an issue which needs to be clarified. In this presentation we discuss the example of a few structures which are promising in terms of separation properties, but also in terms of efficiency under moisture. We first studied the hydrothermal stability of the PBAs by XRD, thermodiffraction and nitrogen adsorption. Based on the experimental and simulated adsorption isotherms, it is indeed possible to calculate the Henry's constants of the sorption systems which can be seen as a predictive tool of separation efficiency. As an example, in Figure 1, we show two consecutive adsorption isotherms of water on the lacunary-containing $Co[Co(CN)_6]_{2/3}$ compound determined at 303 K. [3] The difference of affinity at low relative pressure is clear and suggests that the hydrophilic/hydrophobic balance can be precisely tuned by preadsorbing water species on the unsaturated metal centers of this PBA. If the pristine PBA appears as a truly hydrophobic material, saturating the CUS with water highly enhances its hydrophilicity as anticipated by Balsameda in the past. [4] Further water sorption cycles are superposed with the 2nd sorption cycle showing that this material is particularly robust to water atmosphere. This capability makes this material a very promising candidate for hydrocarbons separation in a humid atmosphere. Examples of highly efficient humid hydrocarbons separation will be also presented.

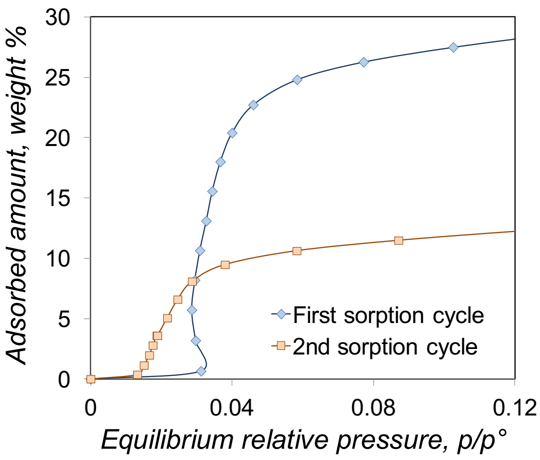

Figure 1. Adsorption isotherms of vapors at 303K by the Prussian Blue Analogue $(CoCo(CN)_6$.

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OW2

Coarse-grained model of sodium polyacrylate in montmorillonite

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The presence and dissemination of numerous pollutants in the soils is a problem of great importance. Natural organic matter is known to play an important role in the mobility of cations (metal ions, radionuclides) in soils. It has been shown that several humic acids seem to have the same charge and also the same diameter of approximately 2 nm. Polyacrylic acid (5100 g/mol) can be considered as a good analogue of these humic acids concerning size and charge in solution [1]. We propose in this study to investigate the interaction of sodium polyacrylate with a clay, the montmorillonite. For that purpose, we first derive coarse-grained models of the polyelectrolyte starting from atomistic simulations. Two models are proposed, which differ from their complexity : in the first one, each monomer and its counterion are described by a neutral bead, and in the second one counterions are explicitely taken into account. We compare the predictions of both models concerning the gyration radii, the self-diffusion coefficients as a function of the size of the chain. We also investigate the interaction of these PAA model chains with a coarse-grained model of montmorillonite which has been built previously [2]. The behaviour of both models is discussed in the light of atomistic simulations [3].

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OW3

Fenton treatment using iron nanoparticles supported on activated carbon from banana spike: Rhodamine B removal and treatment of dyeing wastewater

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In order to treat the textile effluents, research efforts have concerned advanced oxidation processes both at laboratory and industrial scale. Among these processes, the Fenton one is financially attractive because it requires the use of Fe^{2+} or Fe^{3+}/H_2O_2 reagents to generate the $OH^{\bullet}$ hydroxyl radicals [1]. In order to avoid the recovery of iron ions in the treated effluent, we have focused on the use of iron nanoparticles supported on activated carbon (AC) as a Fenton catalyst.

Iron nanoparticles supported on activated carbon (AC) were prepared by the calcination of a microporous/mesoporous activated carbon, obtained from banana spike (S_{BET}= 896 m^2/g), and impregnated with iron sulphate solution. The catalysts referred to AC@Fe/3, AC@Fe/7 and AC@Fe/11 were prepared from impregnation ratio (Fe iron mass ratio to the AC mass) of 3%, 7% and 11%, respectively.

The catalysts were characterized by N_2 and CO_2 adsorption-desorption at 77 and 273 K, respectively, for their pore size distributions, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM) coupled to energy dispersive spectroscopy, and Infrared Spectroscopy (IR). The presence of iron-based nanoparticles dispersed in the porosity was demonstrated by SEM and TEM observations, and the PSDs. The nanoparticles were identified as wüstite (FeO) by XPS. The TEM and PSDs of these three catalysts have revealed that iron nanoparticles (14-30 nm) are located mainly in the mesopores.

The catalysts (0.2 g/L) were firstly studied for the removal of Rhodamine B (red dye at C_0=50 mg/L in 200mL, pH=4.2) in batch aqueous solution by single adsorption and by the heterogeneous Fenton degradation process (in the presence of H_2O_2, 8 mmol/L). The AC@Fe/11 catalyst was used to determine the effect of the initial H_2O_2 concentration (4-10 mmol/L), the catalyst dose (0.2-0.4 g/L, the initial dye concentration (30-100 mg/L), pH (2-8) and temperature (20°C, 28°C, 40°C) on the dye removal (measured by spectrophotometry).

In a second step, the optimization of the Fenton treatment of a textile wastewater from handicraft loincloths dyeing (Bamako, Mali) was studied by using the AC@Fe/11 catalyst. The response surface methodology (RSM) was used to optimize the effects of three independent parameters (catalyst dose, H_2O_2 concentration, and initial total organic carbon (TOC) concentration) on the treatment efficiency assessed by the rate of TOC (Total Organic Carbon) reduction.

The AC@Fe/11 catalyst has allowed to achieve 93% of solution discoloration compared to 87.4% for AC/Fe/7 and 78.5% for AC@Fe/3 after 180 min reaction in batch at pH 4.2. Indeed, the best catalytic efficiency of AC@Fe/11 is attributed to its highest amount and appropriate dispersion of the iron nanoparticles in the porosity. Indeed, at low amounts of AC@Fe/11 (0.27 g/L) and H_2O_2 (8 mmol/L), 96.1% of Rhodamine B discoloring rate and 64% TOC reduction were obtained after 180 min at pH 4,2. Also, this catalyst was recycled for further reuse giving abatment rate around 73% after the 2nd cycle. After four cycles the iron loss has been estimated to 15.7% indicating still a potential activity for the Fenton reactions. The 70.7% removal of nitrogen and the disappearance of the benzene rings has proved the Rhodamine B degradation and its mineralization. The promising catalytic activity of AC@Fe/11 for Rhodamine B removal has suggested its use for the treatment of a real effluent such as dyeing waste water.

The optimal conditions for the treatment of this waste water (from Bamako handicraft textile dyeing) have been found at 2 g/L catalyst, 16.73 mmol/L H_2O_2 and 99.83 mg/L initial TOC leading to a prediction of 90.2% reduction of TOC. In these experimental conditions, a rate of degradation of 90.4 % was measured in agreement with the response model equation (second degree polynomial equation) determined by RSM. This demonstrates that the Fenton process using AC@Fe/11 catalyst is a viable treament.

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Importance of illite for Tl uptake in soils

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Thallium (Tl) commonly occurs in the environment as monovalent Tl^{I} and, to a lesser extent, as trivalent Tl^{III}. The clay mineral illite has long been assumed to be a key sorbent for Tl^{I} in soils and sediments. This hypothesis was based on the similarity of the ionic radius and hydration energy of the cations Tl^{+} and Cs^{+}. For the latter, highly specific adsorption at the frayed edges of illite and fixation in the illite interlayer has been documented [1, 2]. First direct spectroscopic evidence for the sequestration of Tl by illite was presented in a study on the speciation of Tl in geogenically Tl-rich soils from the Swiss Jura mountains (Erzmatt) [3]. In a laboratory study, we recently confirmed the high affinity of Tl^{I} for illite and derived selectivity coefficients for Tl-Na, Tl-K, Tl-NH_4 and Tl-Ca in the framework of an established 3-site cation exchange model [4]. To further assess and constrain the role of Tl^{I} adsorption and fixation by illite in soils, we examined the solubility and exchangeability of geogenic Tl and freshly spiked Tl^{I} in these Erzmatt soils.

The extraction of 36 topsoil samples with geogenic Tl contents ranging from 3 to 1000 mg/kg with 10 mM $CaCl_2$ and with 1 M NH_4-acetate showed that 3.5±1.8% of the geogenic Tl was NH_4-exchangeable and revealed a nearly linear relationship between soluble Tl (10 mM $CaCl_2$) and exchangeable Tl (1 M NH_4-acetate). Tl L_{III}-edge X-ray absorption spectra of 12 soils suggested that most of the geogenic Tl was Tl^{I} associated with illite. These findings indicate that a major fraction of the geogenic Tl was fixed in the interlayers of illite (or other micaceous phyllosilicates) over the time of soil formation, and that short-term Tl solubility was controlled by the minor fraction of exchangeable Tl.

To assess the exchangeability and solubility of freshly spiked Tl^{I}, six soils with geogenic Tl contents from 3 to 300 mg/kg were reacted with up to 1000 mg/kg Tl^{I}. The subsequent extraction of the spiked soil samples with 10 mM $CaCl_2$ and 1 M NH_4-acetate confirmed the suitability of these extracts to determine the solubility and the pool of exchangeable Tl. The recovery of only about 80% of the freshly spiked Tl in the 1 M NH_4-acetate extracts may have been due to the short extraction time or due to rapid fixation of a fraction of the Tl^{I} in the interlayers of clay minerals.

Using the 3-site cation exchange model for Tl adsorption onto illite, the solubility of the exchangeable Tl could be reasonably reproduced for both geogenic and spiked Tl. The calculations indicated that exchangeable Tl^{I} was mostly bound at the frayed edges of illite-like clay minerals, where competition with K^{+} and NH_4^{+} prevails, and that the importance of planar sites was limited due to the strong adsorption competition of the bivalent cations Ca^{2+} and Mg^{2+}.

Together, our results obtained from soils with geogenic and spiked Tl confirmed that illite (and other micaceous minerals) affect the fate and impact of Tl in soils via exchangeable Tl adsorption (short-term) and structural Tl fixation (long-term).

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OW5

Polycyclodextrin-clay composites: Regenerable dual-site sorbents for Bisphenol A removal from treated wastewater

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Many sorbents have been designed for the removal of micropollutants from treated wastewater (TWW), however, sorbent implementation is usually limited due to the presence of effluent organic matter (EfOM) and sorbent regeneration. In this study, we directly addressed these two challenges by designing regenerable dual-site composite sorbents for the simultaneous removal of a micropollutant, bisphenol A (BPA), and EfOM from TWW. A composite based on polymerized β-cyclodextrin modified with a cationic group (pCD$^+$) adsorbed to montmorillonite clay (pCD$^+$-MMT), was designed and its structure characterized. The composite was tailored to target BPA through hydrophobic size inclusion in β-cyclodextrin cavities, while removal of the anionic EfOM compounds was achieved by the cationic group. Equilibrium and time-dependent adsorption studies indicated that the simultaneous removal of BPA and EfOM, from wastewater, by the dual-site pCD$^+$-MMT was as high as the removal of each pollutant separately. The removal of BPA by pCD$^+$-MMT was more rapid than its removal by granular activated carbon and even faster than its removal by a mono-site composite based on pCD^0 (lacking the cationic group) that does not adsorb EfOM. The planar conformation of pCD$^+$ on the clay surface, in comparison to the globular one of pCD^0, can explain the more rapid removal of BPA by pCD$^+$-MMT. The simultaneous filtration of BPA and EfOM from wastewater by pCD$^+$-MMT columns, was demonstrated. Furthermore, highly efficient, in-column regeneration was obtained by selectively eluting EfOM and BPA, with brine and alkaline solution, respectively. This study highlights the potential to design novel dual-site composites as selective and regenerable sorbents for advanced wastewater filtration.

Influence of magnetite stoichiometry on the binding of emerging organic contaminants

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While the magnetite stoichiometry (i.e. Fe(II)/Fe(III) ratio) has been extensively studied for the reductive transformation of chlorinated or nitroaromatic compounds, no work exists examining the influence of stoichiometry of magnetite on its binding properties. However, if its stoichiometry plays a dominant role in its ability to reduce contaminants [1-3], this should also theoretically affect the proportions of ≡Fe(II)-OH/≡Fe(III)-OH surface sites and, therefore, its binding capacity for emerging contaminants such as nalidixic acid (NA), an intensively used quinolone antibiotic. This hypothesis was tested by conducting NA adsorption experiments ($[NA]_{tot}$ = 20µM) on magnetites with various stoichiometries (MX, with X = 0.50, 0.44, 0.42, 0.40, 0.33 and 0.24; 50 $m^2 L^{-1}$) as a function of pH ([NaCl] = 10 mM) under N_2 atmosphere (anaerobic chamber). Different magnetites were prepared from synthesized stoichiometric magnetite (M0.50) by applying one (M0.44) or three (M0.40 / M0.42) washing steps with N_2-purged ultrapure water, by adding known amounts of H_2O_2 (M0.42 and M0.33) or by exposition to air during 24h (M0.24). All magnetite particles were ~10 nm in diameter (TEM analysis) and exhibited a surface area of ~90 $m^2 g^{-1}$ (N_2-BET).

Figure 1a shows NA adsorption to all magnetites versus pH. NA adsorption to M0.42 prepared either by the washing procedure or by using H_2O_2 does not significantly differ, so the data were merged in Fig. 1a. NA adsorption to M0.24, M0.33 and M0.40 is similar but drastically increases with magnetite stoichiometry for Fe(II)/Fe(III) > 0.40. However, at low pH (e.g. pH = 6), NA adsorption to all magnetites is similar. Because of Fe(II) dissolution, the amount of bound-Fe(II) in magnetite can vary depending on pH, as shown in Figure 1b by plotting corrected Fe(II)/Fe(III) ratio from dissolved Fe(II) ($(Fe(II)/Fe(III))_{bound}$). All magnetites show similar $(Fe(II)/Fe(III))_{bound}$, hence similar adsorption capacity for NA.

Previous studies showed that exposing non-stoichiometric magnetite (i.e. low Fe(II)/Fe(III) ratio) to a source of Fe(II) can restore the 0.5 ratio (i.e. perfectly stoichiometric magnetite) [1,2]. Known amounts of dissolved Fe(II) were added to M0.40 suspensions in order to reach the same Fe(II)/Fe(III) ratio as M0.42, M0.44 and M0.50 to test wether magnetite recharge can restaure NA adsorption behavior. This is indeed veryfied (Fig. 1a), Fe(II)-ammended M0.40 showing similar $(Fe(II)/Fe(III))_{bound}$ than other magnetites (Fig.1b).

This study, for the first time, demonstrates that the stoichiometry strongly affects the capacity of magnetite to bind not only NA but also, according to additional experiments, Flumequine (another quinolone antibiotic), salicylic acid, humic acid and dissolved silicates (see [4] for more details). These results might have strong implication on the fate of emerging contaminants, especially in Fe-rich subsurface environments or temporary flooded soils (e.g. wetlands experiencing redox potential fluctuation) where magnetites of differential composition and stoichiometry may exist depending on the local redox and chemical conditions.

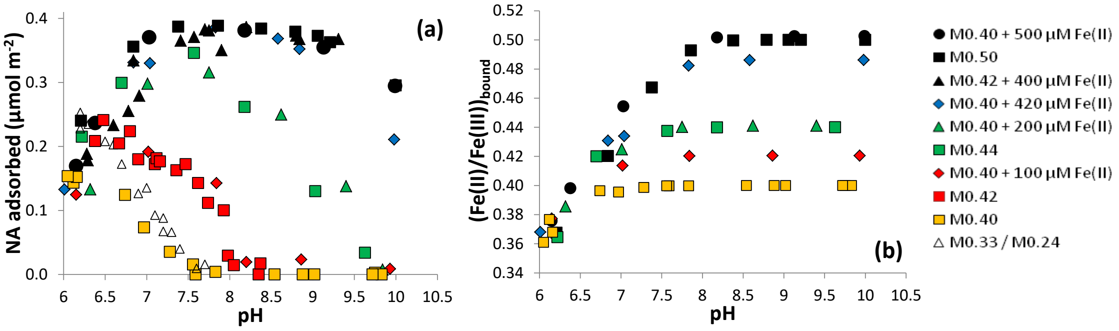

Figure 19: (a) NA adsorption data versus pH for 50 $m^2 L^{-1}$ suspensions of M0.24, M0.33, M0.40, M0.42, M0.44, M0.5 and Fe(II)-amended M0.40 versus pH in a 10 mM NaCl + 20 µM NA solution, after 24h reaction time. (b) calculated $(Fe(II)/Fe(III))_{bound}$ in the corresponding experiments.

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KN8

The lability of nanoparticulate metal complexes at a macroscopic interface: the reaction layer concept revisited

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Complexing nanoparticles (NPs) exhibit unique reactivity features that arise from the spatial confinement of ligand sites to the particle body. The effects are most pronounced for the case of soft charged nanoparticles (NPs) interacting with oppositely charged ions: in such case, reaction rates may even be orders of magnitude greater than their molecular counterparts.[1] Metal binding to the reactive sites of NPs takes place within the local environment of the NP body, where the physicochemical conditions can be very different from that prevailing in the bulk aqueous medium. In environmental and biological contexts, the typical parameter of interest is the rate of interconversion between the free metal ions in the bulk medium and their complexed forms, with a view to interpreting signals from dynamic speciation analysis and predicting bioavailabilities.[2] Such strategies have a differentiated meaning in the presence of soft NP complexants, since part of the NP-'bound' metal may be in the form of free ions within the NP body.

We adopt a differentiated approach that considers the role of the chemodyamics of inner-sphere metal complexation at the intraparticulate level,[3] in conjunction with the particle/medium exchange of the reactive target species (typically the free metal ion), coupled with diffusion towards a macroscopic reactive interface.[4] In doing so, we introduce the concept of an operational reaction layer at the macroscopic interface and explore the significance of partial size exclusion of the NP body therefrom.[4,5] The interpretation is drawn to the level of the operational (bioavai)lability of nanoparticulate metal complexes at macroscopic reactive interfaces, e.g. a dynamic speciation sensor or an organism. The utility of the developed theoretical framework is illustrated by confrontation with experimental data.

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OW7

Coupled analyses of changes in iron oxide mineralogy and reducibility during ferrous iron catalysed transformation of ferrihydrite to goethite and magnetite

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Ferrihydrite is a poorly crystalline ferric iron oxide that transforms into crystalline goethite and/or magnetite in the presence of Fe^{2+}. This transformation process has several important implications: it largely affects i) the thermodynamic favourability of using the oxide as terminal electron acceptor in anaerobic microbial respiration, ii) the (bio)availability of mineral-associated inorganic contaminants as well as trace minerals, and iii) the reduction potential of oxide-associated Fe^{2+} and thus its reactivity towards reducing inorganic and organic pollutants. Obtaining a fundamental understanding of ferrihydrite transformation into more crystalline iron oxides is therefore important to assess the impact of this process both on biogeochemical redox cycles and pollutant redox dynamics.

In this work, we link changes in iron oxide mineralogy to changes in iron oxide reducibility during Fe^{2+}-catalysed transformation of ferrihydrite to goethite and magnetite (reaction equations are shown in Figure 1). We studied these transformations over a range of solution pH (i.e., pH 6.5 to 7.5) and at two Fe^{2+} concentrations (1 mM and 5 mM, both at pH 7.0) by combining three novel experimental approaches: 1. We coupled the transformation experiments to automated base titrators operated in pH stat mode to determine the number of protons (H^+) released during the transformations and, thereby, the amount of magnetite formed. 2. We analysed changes in iron oxide mineralogy by powder X-ray diffraction (XRD) analysis in which we fitted mass fractions of the poorly crystalline ferrihydrite using the 'partial or no know crystal structure' approach in Rietveld refinement. 3. We determined changes in iron oxide reducibility by mediated electrochemical reduction (MER).

Ferrihydrite transformed to magnetite at pH ≥ 7 (5 mM Fe^{2+}) within hours. Conversely, goethite was formed at lower pH < 7 (5 mM Fe^{2+}) and at lower Fe^{2+} of 1 mM (pH 7.0) over days to weeks. Consistent with the reaction equation for ferrihydrite transformation to magnetite (Figure 1), the number of H^+ released was close to stoichiometric relative to oxide Fe^{3+} in experiments in which magnetite formed as major phase. MER analysis showed a decrease in iron oxide reducibility that followed the extents to which ferrihydrite transformed to goethite and magnetite. The three approaches therefore allowed linking changes in iron oxide mineralogy to changes in iron oxide reducibility.

This work provides new insights into Fe^{2+}-catalysed transformation dynamics of ferrihydrite to goethite and magnetite. We will highlight the implications of our findings both for biogeochemical and pollutant redox processes.

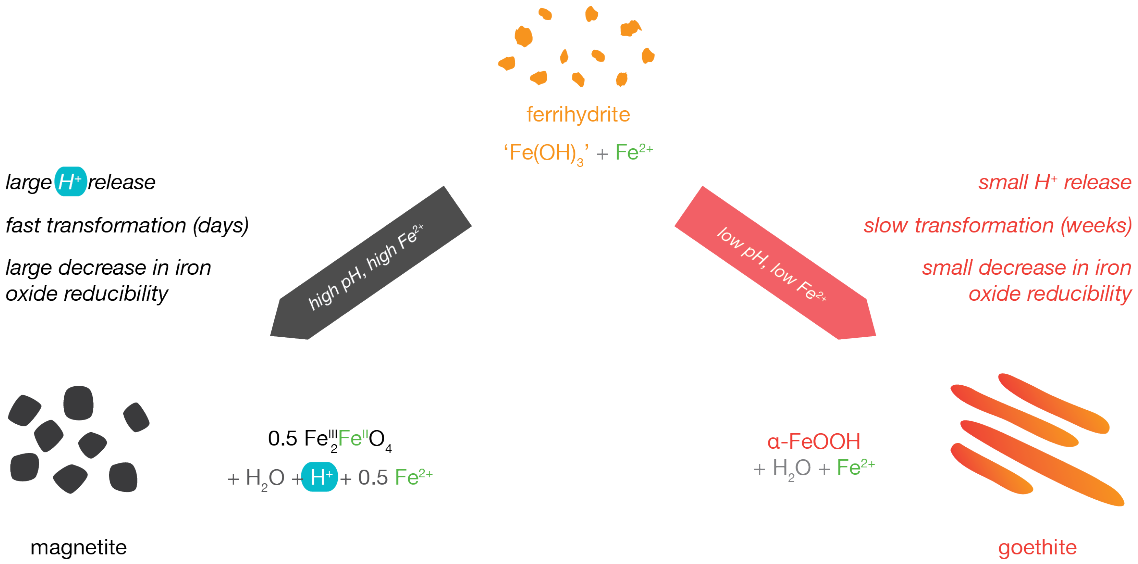

Figure 20: Schematic illustration of ferrihydrite transformation to magnetite and goethite.

OW8

Contribution of soil active components to the control of heavy metal speciation and modeling

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Soil active components including soil organic matter, clay silicates, metal hydroxides and microorganisms, which have large surface area and are often electrically charged, are considered as important surfaces to immobilize heavy metals by precipitation, adsorption or (bio)transformation et al. The development and application of in-situ measurement, micro-examination and element tracing technologies significantly accelerated the development of studies with related to heavy metal interactions with soil active components. The in-situ measurement and the greatly improved understanding of soil microscopic properties based on microscopic spectrum technology at molecular level laid solid foundation for the rapid understanding of immobilizing heavy metals in soil and development of soil remediation. Quantum chemistry calculation combined with spectral information has greatly enhanced the understanding of these processes at the molecular level. Meanwhile, the bioavailability and toxicity of heavy metal in soil is mostly decided by its speciation and not its total amount. Therefore, it is necessary to make accurate assessments of heavy metal speciation. The various types of models have been developed to calculate chemical speciation or the distribution of chemicals over all relevant forms on different soil active components. Fundamental understanding of these reactions and processes at the atomic, molecular, and microscopic levels is essential for remediation of heavy metal pollution in soils, sustaining and enhancing soil health, which includes human health, on a global scale.

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Modeling lung surfactant interactions with benzo[a]pyrene

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Degradation of natural environment, in particular air pollution, is one of the prices we pay for improved quality of life, provided by civilizational growth in the Western world. Although a significant reduction of air pollution has been recorded in Europe in the last decades, still in many regions air quality is low and potentially harmful to human health and ecosystems. Among many ingredients of air pollution, particulate matter (PM) has long been recognized as one of the most troublesome. It is a mixture of various chemical species suspended in the air, whose particles cover a broad range of sizes. Among them, those with mean aerodynamic diameter smaller than 10 μm can pass to lower parts of respiratory system and are traditionally classified as thoracic particles. Particles with a diameter smaller than 2.5 μm are called respirable particles and can penetrate through the airways to the gas-exchange surface.

One of the most dangerous components of respirable PM are the polycyclic aromatic hydrocarbons, in particular benzo[a]pyrene (BaP), which is a potent carcinogen. It forms during incomplete combustion of all organic materials, e.g. coal, wood, or automobile fuels, but also tobacco or foods. In human body BaP is metabolized to highly reactive species, such as diol epoxide, quinone or radical cation, which react with DNA, leading to DNA damage, an important first step in carcinogenesis. According to the latest report on air quality published by European Environment Agency, about 90% of European cities' inhabitants are exposed to BaP levels exceeding the World Health Organization's air-quality guidelines.

At the surface of gas exchange, the first barrier any inhaled substance has to cross before entering the body is the lung surfactant (LS). It is a surface active monolayer which lines the air-water interface on the surface of alveoli. Its main function is the reduction of surface tension (γ) at the interface. On inspiration, this reduces the work needed to expand interfacial area, while on exhalation, it prevents alveolar collapse.

In this study we inspect the interactions of LS models with a dangerous air pollutant, benzo[a]pyrene. DPPC, POPC and their 1:1 mixture are used as LS models. Pressure-area isotherms are employed to study macroscopic properties of the monolayers. We find that addition of BaP has a condensing effect, manifested by lowering the values of surface pressure and shifting the isotherms to smaller areas. Atomistic details of this process are examined by means of molecular dynamics simulations. We show that initially BaP molecules are accumulated in the monolayers. Upon compression, they are forced to the headgroups region and eventually expelled to the subphase. BaP presence results in reduction of monolayer hydration in the hydrophilic region. In the hydrophobic region it induces increased chain ordering, reduction of monolayer fluidity, and advances transition to liquid condensed phase in DPPC system.

OW10

Bursting mechanism of emulsion based liquid sheets: anti-drift application for agricultural sprays

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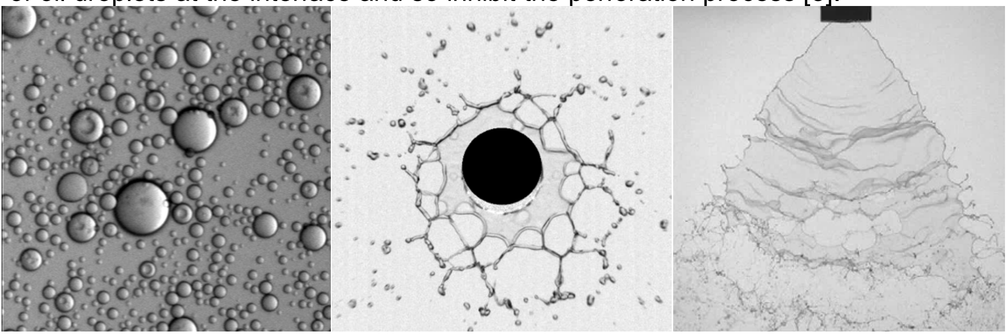
One of the major environmental issues related to spraying of pesticides on cultivated crops is the drift phenomenon. Because of the wind, small droplets may drift away from the targeted crop and cause contamination. One way to reduce the drift is to control the spray drop size distribution and reduce the proportion of small drops. In this context, anti-drift additives have been developed, including dilute oil-in-water emulsions. Although being documented, the effects of oil-in-water emulsions on spray drop size distribution were not well understood. The objective of this work is to determine the mechanisms at the origin of the changes of the spray drop size distribution for emulsion-based sprays. Agricultural spraying involves atomizing a liquid stream through a hydraulic nozzle. At the exit of the nozzle, a free liquid sheet is formed, which is subsequently destabilized into droplets. With a model experiment, based on the impact of a single tear of liquid on a small target, we investigate the destabilization mechanisms of liquid sheets and compare the results obtained to the drop size distribution of sprays produced with agricultural noozles [1]. Emulsion-based liquid sheets are destabilized through the nucleation of holes within the sheet that perforate the sheet during its expansion. We propose the perforation mechanism as a sequence of two necessary steps: the emulsion oil droplets (i) enter the air/water interface, and (ii) spread at the interface [2]. We show that the formulation of the emulsion is a critical parameter to control the perforation. Thin-film forces such as electrostatic or steric repulsion forces stabilize the thin film formed between the interface and the approaching oil droplets preventing the entering of oil droplets at the interface and so inhibit the perforation process [3].



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Aerosol scavenging by droplets: impact of rear capture for low inertia aerosol and moderate to transitional Reynolds number

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Scavenging aerosol particles by droplets is an efficient way of removing solid particles from gases. When a droplet goes through a cloud of aerosol, the main aerosol collection mechanisms that occur are direct inertial impaction of aerosols on the drop surface, Brownian diffusion of aerosol particles to the drop surface, diffusiophoretic and thermophoretic attraction or repulsion for evaporating or condensing droplets, and deposition due to various electrical interactions. Not only do these processes act simultaneously, but they also act in interaction with the aerosol concentration field, with the temperature field and with the water vapor concentration field around the drop, all depending on the flow regime around and inside the drop. Among the various collection mechansisms that occur, the rear capture mechanism is one of the least documented one: this phenomenon occurs when an aerosol particle is caught in the rear standing eddy that appears in the wake of the droplet for $Re_d > 20$, and was first suggested by [1]. This eddy presents its maximum elongation for $Re_d \approx 200\text{-}300$, and then degenerates into a periodic detachment. Consequently, observing experimentally that the scavenging efficiency of low inertia aerosols increases suddenly for Red>100 and decreases again for Red>300 - which was also partly observed numerically by [1] – Pruppacher [2] attributes this sudden upsurge of scavenging efficiency for this range of Reynolds number to the apparition of the rear capture mechanism. However, there is so far no true evidence of a relationship between this upsurge of capture efficiency and the mechanism of rear capture.

In a former study[3], we used microphysical modeling to compute precisely the drop collection efficiency for aerosol particles around the Greenfield gap which are submitted to both drag force and Brownian motion, for droplets falling in quiescent air at moderate Reynolds number ($Re_d \leq 100$). In this approach, a Lagrangian procedure is used to model the semi-stochastic trajectory of aerosols, while the coupled laminar flows inside and outside the droplet are computed thanks to an eulerian finite volume approach, taking into acount interfacial effects. In the present work, we now use the same procedure to examine in details the role of rear capture on the total collection efficiency, for drop Reynolds number ranging between 20 and 400 and for aerosol particles submitted to both Brownian motion and inertia only. Simulation data are used to illustrate the trajectory of aerosol particles around the drop and their interaction with the wake of the drop, leading eventually to ejection or to rear capture. The total contribution of rear capture on scavenging is then derived as a function of Reynolds number and aerosol Stokes number.

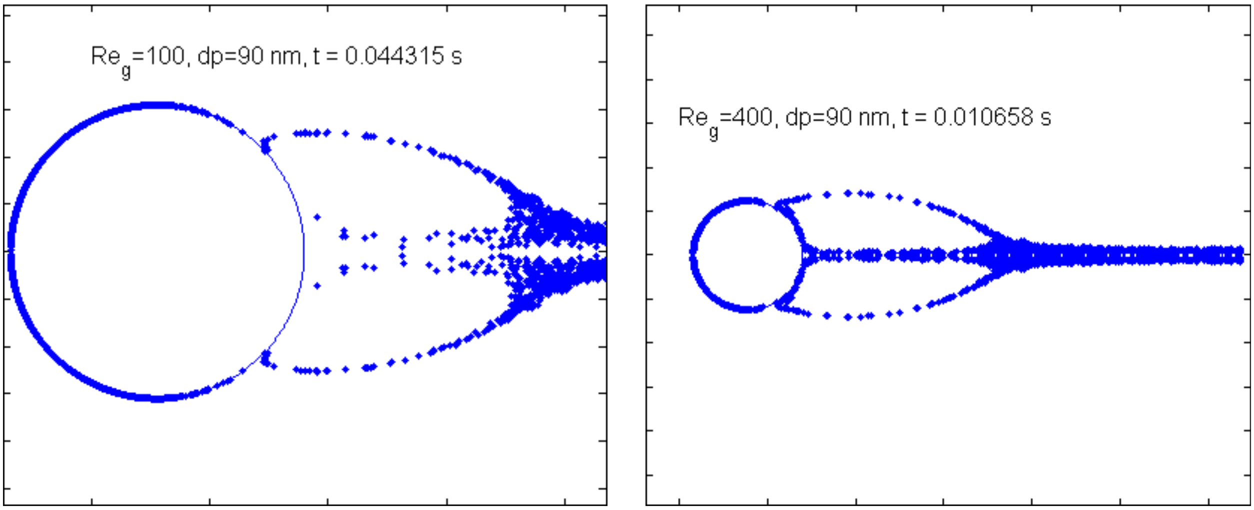

Figure 21: aerosol particles of 90nm aerodynamic diameter interacting with the wake of the droplet for Re = 100 and 400 respectively

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OW12

Interfacial behaviour of plant proteins

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Challenges of public health and sustainable development require replacing in food producs animal proteins by plant proteins. In this optics, it is crucial to understand the structure and kinetic of formation of a film of plant proteins film in order to improve the control of emulsions and foams stabilized by these proteins.

In this talk I will present experimental results on the interfacial properties of wheat gluten and sunflower proteins. Thanks to a combination of tensiometry, viscoelasticity and ellipsometry, a consistent and rational physical picture of the dynamics of the interfacial properties is achieved.

For gluten proteins, a time-concentration superposition of the data is evidenced whatever the subphase concentration, which reveals that protein adsorption at the interface is dominated by bulk diffusion. We propose a consistent physical picture of the multistep diffusion-controlled irreversible adsorption of the gliadin proteins at an air/water interface [1]. Our data shows clearly three different regimes for the film formation (Figure 1). In the first regime, the film elasticity and surface protein concentration increase concomitantly due to the progressive coverage of the interface by proteins. In the second regime, an increase of the dissipative viscoelastic properties is associated to an anomalous evolution of the optical profile that we attribute to conformational changes of the proteins at the interface induced by surface pressure. In the last stage, at even higher surface pressure, the optical profile is not modified while the elasticity of the interfacial layer dramatically increases presumably due to the film gelation as the result of the formation of intermolecular bonds. Overall all our experimental results indicate that wheat gluten displays behaviour typical of soft proteins due to their structural flexibility.

Sunflower proteins, by contrast, can be considered as hard proteins, and as such, do not reorganize once adsorbed at an interface and display a simpler film formation dynamics. In addition the failure at high concentration of the time-concentration superposition of the tensiometry and viscoelastic data strongly suggest an aggregation process.

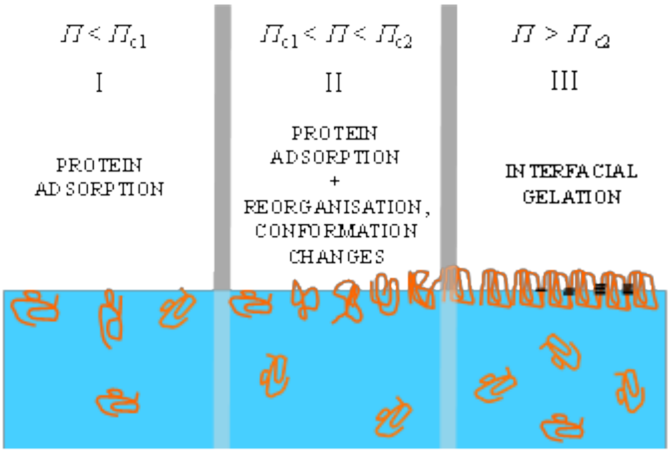

Figure 22: Scheme of the three interfacial regimes identified thanks to structural and rheological measurements of a soft wheat protein air/water interface. The three regimes are defined by the interfacial pressure

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KN9

Cadmium binding and formation of nano-sized particles with humic acid extracted from deep sedimentary groundwater

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Humic substances (HSs) are ubiquitous in various environments and play an important role for the fate of pollutants. Deep underground environment is not an exception, although the properties of HSs there are largely unknown due to their limited availability. Recently, we reported the physicochemical and ion-binding properties of HSs extracted from sedimentary groundwater at -250 m below ground surface of the Horonobe underground research laboratory operated by the Japan Atomic Energy Agency, pointing out their particularity, compared with HSs from various surface and shallow subsurface environments [1, 2]. The aim of this talk to supplement the preceding study by demonstrating the formation of nano-sized particles upon cadmium (Cd^{2+}) binding to the humic-acid (HA) fraction of the Horonobe HSs.

The extraction and purification of the Horonobe HSs is reported elsewhere together with their elemental compositions, carbon speciation by ^{13}C NMR, sulfur speciation by sulfur K-edge X-ray absorption near-edge structures (XANES), size distributions by flow-field flow fractionation (Fl-FFF), UV/Vis and fluorescence spectra [1, 2]. In summary, the Horonobe HSs consisted of relatively small organic molecules rich in aliphatic carbons and reduced sulfurs like thiol. Cluster analysis suggested that the Horonobe HSs are statistically different from the surface HSs. The H^+ and Cu^{2+} binding to the Horonobe HSs was studied by potentiometric titration, revealing that at relatively low pH these ions bound to chemically homogeneous carboxylic-type groups with 1:1 stoichiometry. This also explained the weak binding of Cu^{2+} to the Horonobe HSs, compared with that to the surface HSs.

Cadmium binding to the Horonobe HA (HHA) was studied by potentiometric titration with a Cd^{2+} selective electrode, Cd K-edge X-ray absorption spectroscopy, and Fl-FFF coupled with inductively coupled plasma mass spectrometry (ICP-MS). The Cd^{2+} binding isotherms to HHA measured at pH 4, 6, and 8 exhibited the presence of strong buffering, where the Cd^{2+} binding amounts steeply increased within short ranges of its free concentration. The starting concentrations of this buffering tended to decrease with an increase of pH. The presence of the buffering suggested the formation of a solid phase containing Cd^{2+}, which was tested by Cd K-edge XANES and extended X-ray absorption fine structure (EXAFS). The EXAFS oscillation and their Fourier-transformed amplitudes exhibited systematic changes as a function of the Cd^{2+} loading and pH. By comparing them with the EXAFS of standard compounds with known structures suggested the formation of CdS at relatively high Cd^{2+} loadings and pH (Figure 1). The comparison of the HHA and Cd^{2+} fractograms obtained by the Fl-FFF-ICP-MS further revealed that the majority of Cd^{2+} was eluted at the size ranges larger than that of HHA. This also suggested the formation of a relatively large solid phase. In the presentation of the conference, I will present the quantitative structural information obtained from the theoretical fitting of the Cd^{2+} EXAFS and discuss possible causes for the formation of CdS nano-sized particles upon interaction with HHA.

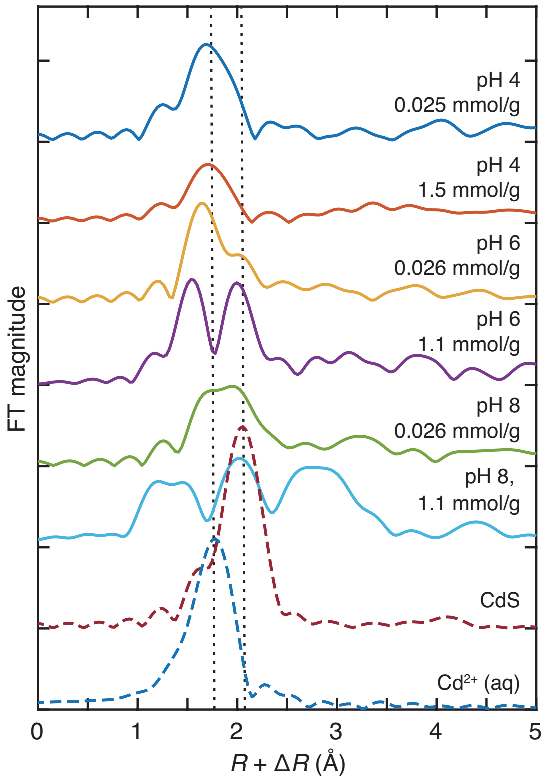

Figure 23**: Fourier-transformed magnitudes of the EXAFS spectra of Cd2+ bound to HHA together with those of standard compounds (Cd^{2+} aq. ion and CdS (s).**

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OW13

Zinc, Zinc-complexing ligands and humics in corals: developing a method to assess historical records of metal bioavailability

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Understanding how organic complexing ligands dominate the chemical speciation of Zn in seawater is essential to have a quantitative assessment of its bioavailability and its role as a micronutrient. Being able to understand metal bioavailability temporal variability would allow for comprehension about changes through climate change events and long time trends in metal interdependence for enzymatic requirements in phytoplankton. There are analytical methods set up to determine metal concentrations in corals as a proxy for metal concentrations in water using a water/coral partition coefficient. Further, metal isotopes are currently inferred from the metal content in coral samples. Our group has been working with metal concentrations and isotopes in corals. Using our expertise, we want to look further into proxies of metal bioavailability. Methodologically, we determine Zn ligand concentration and binding strengths using ASV, and Zn concentration using an NTA, isotope-dillution ICPMS method. Based on our current work in South East Asia on Zn and its complexing ligands in coastal waters, and with a library of coral samples taken by our team in the region, we set to develop a method that would let us assess the historical records of metal bioavailability in coral samples.

Here we show the most recent advances we have done on the method and preliminary results that correlate ligands with riverine humics in seawater, as these have been found to be the prevalent source of ligands in the region of study. We found very good correlation between L1 and L2 type ligands (logK's ~11 and ~10, respectively, similar to those found in regional waters and global water masses) and humic substances (Suwannee River reference material, from tropical swamps also). We will discuss recent work on (1) determining ligands from humics in corals dissolved in seawater in a non-destructive manner, (2) evaluating coral standards that have oceanic-type humic matter (JCP reference material) and (3) comparing and quantitatively assessing ligands in corals from the region impacted largely by riverine-type humic matter, as this seems to be the apparent dominating ligand source. Finally, our collaborators' concurrent work on organic matter degradation using a combination of satellite-based data and in-situ measurements (Patrick Martin and Nagur Cherukuru) will help us correlate the extent of organic matter export from sources like rivers and peat to the sea with metal complexing ligands.

Further details about the Zn concentrations and complexation by ligands in seawater in South East Asia, as dominated by riverine humics, are provided in a separate presentation.

OW14

Adsorptive fractionation of humic and fulvic acid

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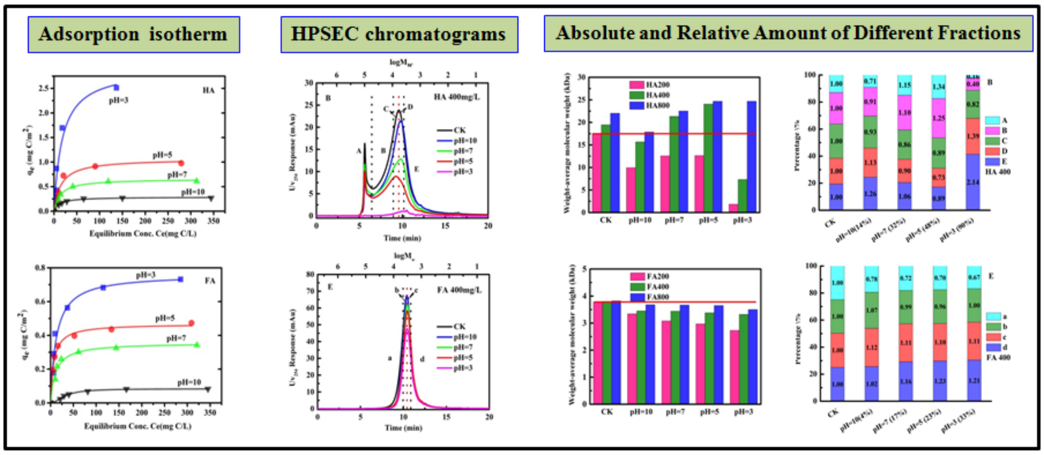
Oxide minerals and humic substances are commonly found nano-sized colloidal particles and they interact with each other in natural environment, which strongly alters the surface properties of both oxide minerals and natural organic matter (NOM). NOM material is very heterogeneous and preferential adsorption takes place during its interaction with minerals. However, so far no consensus regarding the preference has been reached and conflicting statements were made in the literatures. This study investigated fractionation of humic acid (HA) and fulvic acid (FA) during adsorption onto goethite (a-FeOOH) at different pH values and NOM loadings, using total organic carbon (TOC) analysis, UV-Vis spectroscopy, high performance size exclusion chromatography (HPSEC), Fourier transform infrared (FTIR) spectroscopy, and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Compared with that before adsorption, the weight-average molar mass (M_w) of FA decreased, and relatively large particles (3.6-18.2 kDa) were preferred in the adsorption. For HA, the M_w was increased or decreased after adsorption, depending on the initial concentrations and the pH values. At intermediate pH (pH 5, 6), HA particles of the medium size (3.6-12.0 kDa) were preferred in the adsorption, followed with either smaller ones at high HA loading, or bigger ones at low HA loadings. At pH above the PZC of goethite (pH 10), large particles were preferably adsorbed over the smaller ones. For both FA and HA, the specific UV absorbance at 254nm (SUVA$_{254nm}$) decreased strongly after adsorption to goethite, which suggests that NOM particles that are enriched in aromatic structures and acidic reactive groups are preferably adsorbed, which confirms that electrostatic interaction and ligand-exchange complexation are the most important driving force for FA and HA adsorption. The preference for large particles at pH>PZC can be attributed to increased role in hydrophobic interactions when the electrostatic interaction between NOM and goethite is repulsive. The results of FTIR and ^{13}C NMR analysis support the above conclusions.

*Key words :*fractionation, NOM adsorption, goethite, size exclusion chromatography (SEC), weight average molecular weight, SUVA$_{254nm}$,.



OW15

NICA-Donnan modelling of rare earth element binding to humic substances

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The use of Rare Earth Elements (REEs) is currently increasing due to their use in the production of high-tech devices such as liquid crystal displays, communication devices or solar panels among other applications (contrast agents in medicine, electric motors or batteries). The fate of these elements in soils, sediments, and surface waters is largely determined by their binding to reactive components, of which organic matter, metal oxides, and clays are considered important. With the anthropogenic activities involving REEs on the rise, their biogeochemical cycle is being disrupted and an enrichment of certain species has been detected in waters.

Nevertheless, the existent literature about REEs and their environmental effects is scarce. This is one of the main reasons why no regulatory thresholds for REE concentrations and emissions into the environment have been set. However, there is no doubt that REEs have to be acknowledged as new, emerging contaminants wich can get released into the environment via different processes such as weathering, river transport, and estuarine and open ocean processes. The solid solution partitioning and speciation of REEs in soils, sediments and natural waters are of key importance to understand their environmenmtal fate and toxicity.

Thermodynamic models are shown to successfully predict the partitioning and speciation of trace metals in terrestrial and aquatic systems [1]. Considerable progress has been made in the development of mechanistic models for ion binding to reactive components relevant for trace element behavior in natural environments. Ion binding models have contributed largely to the scientific understanding of the behavior and speciation of trace elements in surface waters, groundwaters, and soils..

Binding to natural organic matter is very important for metal speciation in natural systems. Humic substances (humic and fulvic acids) are the most reactive fractions of natural organic matter and have a high affinity for metal ions. However, their reactivity is difficult to study because of their colloidal nature, associated with a heterogeneous affinity distribution. The NICA-Donnan model is one of the advanced models for ion binding to humic substances.At present there are however no NICA-Donnan model parameters for REE binding to humic substances.

Here we derive generic NICA-Donnan parameters for REE based on published data on REE binding to humic- and fulvic acids. The program ORCHESTRA in combination with the parameter estimation program PEST [2] were used to fit the data with the NICA– Donnan model.Choices that were made in the optimization of the parameters will be critacally evaluated. The newly derived model parameters are used to predict the solid solution partitioning in soils using a multi-surface model and compared with measurements in an accompanying study [3]

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Methyl-imogolite: a new hybrid nanotube for water remediation

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Imogolite is a natural aluminosilicate nanotube discovered in 1962 by Yoshinaga and Aomine in volcanic Japanese soils [1]. This nanotube has a monodisperse diameter ranging from 2 and 2.8 nm (depending on its formation and composition) and a polydisperse length (from a few tens of nanometers to several microns) [2]. In recent years, it has been realised that many structural and chemical modifications of imogolite-like structures can be achieved [3,4]. In 2010, Bottero et *al*. succeeded in modifying the tube internal surface by substituting the usual silicon precursor, tetraethoxysilane, with a methyltriethoxysilane [5]. This allows for the formation of a methyl-imogolite (imo-CH_3) with a hydrophilic external surface and a hydrophobic internal surface covered with methyl groups. This nanotube, transparent and dispersed in water even at high concentration, exhibits a 1D hydrophobic polar nanochannel [6].
In 2013, Amara et al. showed that such Janus nanotubes can capture small hydrophobic molecules in water [7]. Later on, we showed that these hybrid nanotubes can stabilise oil-in-water Pickering emulsion and extract a dye from an organic phase [8]. These properties were attributed to the ability of methyl-imogolites cavities to accommodate oil or oil/dye mixtures (figure 1).

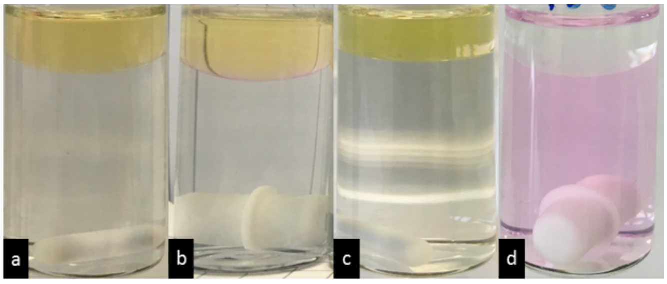

Figure 24: Hexane/Nile Red solutions in contact with water and with imo-CH_3 just after preparation (a) and (b) and three days after stirring (c) and (d)

In this presentation, we will show optimized recipes to produce imo-CH_3 and that it is possible to synthesize new hybrid imogolite nanotube with some of methyl groups substituted by exotic groups. The presence of these new groups is highlighted by the solvatochromic properties of Nile Red. Next, we will assess the water remediation potential of these new nanotubes through comparative trapping of atrazine between hybrid imogolites and activated carbon

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KN10

Electrochemical sensing system for environmental applications

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There are increasing demands for sensing systems that are capable of fast and reliable detection of small quantities of chemical and biochemical targets for different in-field real time environmental applications. As a rule these systems should autonomously operate in a complex media that can contain many interfering species. They are required to possess high sensitivity and sometimes large dynamic range, have low cost and remain functional for extended periods for continuous monitoring applications. These demands are often accompanied by the requirement to the sensing systems to be portable (have low weight and size, small power consumption) and to be equipped with in-built signal processing and data interpretation algorithms to allow using the analytical system outside of specialised laboratories in an automatic mode with no-live operator.

The most of traditional analytical methods, which are used to detect chemical targets, are slow, expensive and require bulky and power hungry equipment demanding dedicated laboratories and highly skilled personnel to operate on it. In this regards electrochemical sensing systems are of particular interest for in-situ autonomous applications as they can be implemented with relatively simple, portable and non-expensive apparatus that can provide for rapid and sensitive measurements in automatic mode. They can detect solid, liquid or gaseous analytes in different mediums with simple operating procedures without or with limited sample pre-treatment that is the essential condition for their implementation outside of the laboratory environment. Emerging microfabrication technologies allowing for manufacturing of micro and nano size electrodes and sensors are boosted an additional interest to electrochemical analytical systems. Miniaturised electrochemical sensors offer a number of advantages over macroscopic devices including increased mass transport and hence improved sensitivity (due to the hemispherical diffusion), reduced *iR* drop and enhanced signal to noise ratio 0.The presented study describes results development of such electrochemical sensing systems by examples of smart system for monitoring of sea water quality [2] and multichannel instrumentation for toxicity screening [3].

The smart sensing system capable of autonomous operation on-board of a robotic fish for monitoring and detection pollution in water area of seaports was developed to provide real time in-situ detection and measurement of contaminants including heavy metal (ions of Cu2+) and phenol derivatives and sea water quality parameters: dissolved oxygen, oxidation-reduction potential (ORP) and sea water conductivity [2]. The sensing system consists of four channel potentiostatic system for quantification of chemical analytes, impedimetric circuitry for evaluation of sea water conductivity and low noise high impedance voltage repeater for measurement of ORP. Multiparametric sensing device was implemented onto a single microfabricated silicon chip with 20×30 mm^2 dimensions. For enhancing sensors sensitivity working electrodes were realized as platinum 30 μm microdics arrays. Selection platinum rather than gold for working electrodes implementation was related to the better stability of Pt to the impact from seawater. Detection limit of pollution was 0.2 μM for cupper and 11.2 μM for phenol.

Multichannel instrumentation for toxicity screening is a part of the third generation miniaturised non-animal high throughput platform for screening the impact of nanomaterial on human health and the environment [3]. In this platform, each channel includes a sensor on silicon chip located inside a flow chamber of the microfluidic system. The sensors are based on biological objects including DNA, miRNA, membrane lipids, single cells and lung, intestine, liver, kidney and placenta cells. Instrumentation provides full control of the multichannel fluidic system and electrochemical examination of the cell-based sensors. The instrumentation allows simultaneous electrochemical measurements independent from other channels and synchronised with the flow controls in the multichannel microfluidic system.

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OW17

Second Harmonic Scattering: a tool to study at the nanometer-scale the molecular adsorption at materials interfaces

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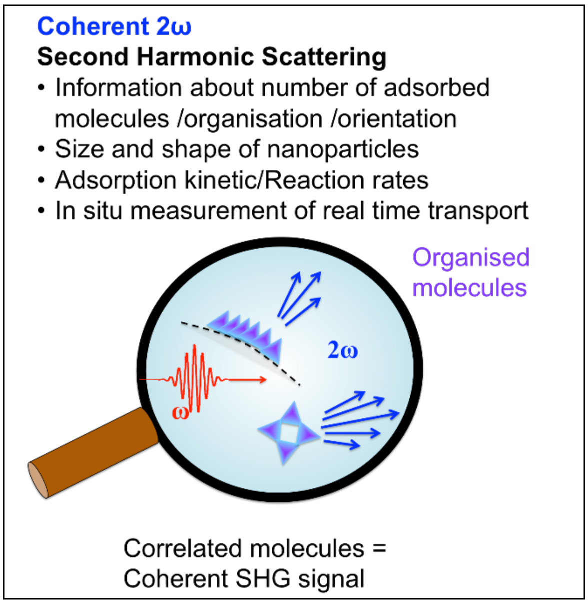
Second Harmonic Generation (SHG) is a nonlinear optical process, in which two photons are converted into one coherent photon at double frequency. This technique, because of its high surface specificity, has been widely used to study "in situ", at the molecular scale the solid/liquid planar interfaces [1]. The use of this process to study other geometries or supramolecular organization is currently a emerging field of research, for example the surface of functionalized colloidal nanoparticles or the internal surfaces of lamellar materials[2,3]. In the case of SHG coming from colloidal objects in bulk solution, the signal is called Second Harmonic Scattering (SHS).



Coherent 2ω

Second Harmonic Scattering

- Information about number of adsorbed molecules /organisation /orientation
- Size and shape of nanoparticles
- Adsorption kinetic/Reaction rates
- In situ measurement of real time transport

Correlated molecules = Coherent SHG signal

Figure 25: The second harmonic scattering technique

After a brief introduction on the basic of these nonlinear optical processes, I will show their interest for the study of molecule/material interactions. The ion exchange and the intercalation of a chromophoric organic molecule in a lamellar material (layered double hydroxide) will be presented. In particular, I will show how the polarization resolved SHS signal can be used to achieved information concerning the equilibrium states of the system: ion exchange capacity, intercalation, orientation of the molecules in the interlayer, and adsorption on external faces. Monitoring of kinetics intercalation will also be presented and discussed.

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OW18

Activitiy coefficients from liquid-vapor interfaces: A molecular dynamics approach for separation chemistry

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The treatment of spent nuclear fuels and the recycling of rare earth elements can be conducted using solvent extraction [1]. In solvent extraction processes, the aqueous phase contains dissolved ionic species up to high concentration. This aqueous phase is in chemical equilibrium with an adjacent organic solvent, which is immiscible in water and contains some amphiphilic extractant molecules (Figure 1). Those extractant molecules enable ion transfer from a mainly polar medium to an apolar solvent.

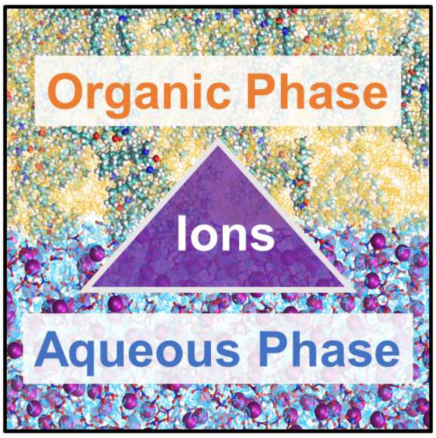

Figure 26: Schematic representation of ion transfer during a solvent extraction process between aqueous (blue) and organic phase (yellow) for separation chemistry. The organic phase contains non-ionic, malonamide-based extractant molecules.

For understanding the driving forces of the ion transfer, it is necessary to understand the properties of liquid-liquid interfaces between organic and aqueous phases, but also to assess the chemical potentials of the involved compounds. Based on the osmotic equilibrium method [2], activities and activity coefficients for aqueous electrolyte solutions, but also for binary solvent mixtures [3] have been successfully calculated. Simulating vapour-liquid interfaces of mixtures and pure solvents by the means of molecular dynamics using polarizable force fields yield activities and activity coefficients of concentrated solutions in good agreement with experimental findings. This approach allows accessing thermodynamic properties in the bulk liquid, while tracing the concentration profiles of all involved species with respect to the interface. In addition, azeotropic compositions can be determined with this approach for binary mixtures.

The great flexibility and the huge potential scope of the osmotic equilibrium method provide access to activity coefficients of complex systems such as aqueous solutions of molecular ions or organic phases. In the case of organic solvent phases used in liquid-liquid extraction, the origin of solvent activity is hardly defined and experiments provide only qualitative results, since aggregate formation leads to non-ideal behavior [4]. This offset neither can be explained by Raoult's law for the solvent nor Henry's law for the solutes. The osmotic equilibrium method, which yields both the thermodynamic properties and the composition of the aggregates at the same time, provides a quantitative and qualitative interpretation of chemical potentials of organic solvent phases and the equilibrium constants for aggregate formation processes.

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Development of a flux DMT with integrated adsorptive stripping voltammetry for free metal ions detection in solution

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Free metal detection in environmental samples is complicated due to the low concentration of free metal ions and the many possible interferences from the matrix components, like the natural organic matter or particles in suspension.

The Donnan membrane technique is a passive sampler device that has been extensivelly used to determine free metal cation concentrations in solution [1]. Usually the device is set two to three days until equilibrium between the internal solution (acceptor) and external solution (sample or donnor) is reached. To shorten this long experimental time a kinetic DMT device was proposed using a strong ligand for the metal ions in the acceptor solution and measuring the flux instead of the equilibrium concentration [2, 3].However the flux DMT presents serious drawbacks on the analytical side due to the need of collecting several aliquotes for analysis, thus requiring more volume of acceptor.

To overcome this problem we propose an integrated electrochemical detection using Adsorptive Stripping Voltammetry to directly quantify the metal in the acceptor solution [4]. In this technique a ligand is added to the solution with the dual function of complexing the metal ion and be adsorbed at the surface of the working electrode, allowing a very low detection limit. For flux DMT it presents the advantage that the adsorbing ligand will also function as the complexing ligand on the acceptor side of the DMT. This proposal is an evolution of the work performed using SWASV to follow the DMT permeation and equilibration time for lead, cadmium and zinc [5].

Development of this new methodology was carried out for Co^{2+} and Ni^{2+} detection with dymethilglioxime and Eu^{3+} detection with cathecol. Results for Co^{2+} and Ni^{2+} are promising, while for Eu^{3+} we observed problems caused by the trivalent ions accumulation into the DMT membrane. Future work is planned to adapt this methodology for use in field systems.

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OW20

Release, and fate of explosive compounds (TNT, RDX, HMX) from discarded munitions in the Baltic Sea

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More than 100,000 tons of conventional munitions were residual or intentionally discarded at various sites throughout the Baltic Sea following WWII. The primary explosive compounds (EC) in these munitions include TNT, RDX, and HMX, which exhibit marked toxicity to biological receptors, in addition to the direct threat of spontaneous or provoked detonation. Within the framework of the Project “Environmental monitoring for the delaboration of munitions on the seabed (UDEMM)”, the current work developed a method for ultrasensitive detection of dissolved EC in seawater using solid-phase extraction and HPLC-ESI-MS analysis. The distribution of dissolved and sedimentary EC were evaluated at a munitions dump site in the Kieler Bucht. Pico- to nanomolar concentrations of EC were detected close to the dump site. We observed gradients in concentration across the Southwest Baltic Sea, consistent with dilution of a point source and suggesting widespread transportation of trace levels of EC. The results of this ongoing study will be discussed in context of environmental conditions that affect EC release and transport. Future efforts to remediate these munition dump sites will need to evaluate how potential EC release during remediation activities may affect the prior steady state balance with natural degradation processes.

POSTER PRESENTATIONS

P01

Direct and double emulsions to capsulate active agents

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An actual problem of colloid chemistry and nanotechnology of scientific and applied importance is the development of promising effective technologies of the encapsulation of functional reagents widely used in practice. In this respect, composite materials are promising that can effectively modify the practical important properties of disperse systems that are widely used in all fields of production, extraction and processing.

One of the most popular for the encapsulation of sensitive reagents are polyelectrolyte capsules obtained by the Layer-by-Layer technique, where oppositely charged polyelectrolytes (polycations and polyanions) are used. However, this method has a number of disadvantages: multistage process involving the layer-wise deposition of polyelectrolyte with multiple intermediate washing procedure after each application, additional dissolution of the core to form a hollow capsule, and subsequent loading of the active ingredients.

In this aspect, of particular interest is the development of a smart encapsulation technology based on direct, double, multiple emulsions. In this connection, it becomes necessary to carry out a series of studies to identify the colloidal chemical features of the formation of interfacial adsorption layers at the liquid interfaces and to establish the features of emulsification with synthetic and natural composite materials.

A modified double emulsion technique was used to capsulate insulin. It was found that preserving the stability and biological activity of insulin during the fabrication can be achieved through the adjustment of the process variables. Insulin-loaded Ch-Xan Gum nanoparticles with improved physicochemical properties with a process yield of 65.6 – 77.46%, and association efficiency of 85.3% were obtained. The resulting capsules were characterized by microscopy, size distribution and Zeta-potential measurements. The release kinetics of insulin was monitored using UV-vis spectroscopy and showed a slow release within 3 hours.

P02

Intensive accumulation of radionuclides by plants and theirs biological circulation

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^{90}Sr and ^{137}Cs are among the large number of artificial radionuclides, which formed from the fission of heavy nuclei. They are chemical analogs of biologically important elements as Ca and K. ^{90}Sr and ^{137}Cs are concentrated by plants in large quantities. Accumulation coefficient of ^{90}Sr and ^{89}Cs can reach 20; ^{134}Cs and ^{137}Cs reach to 2.

The accumulated radionuclides in soil are currently fully involved in the biogeochemical cycles of substance circulation through the food chain and reach humans. Nowadays, artificial radionuclides, particularly ^{90}Sr and ^{137}Cs are found in the body of the inhabitants of the planet, including human.

The intensity of the radionuclides migration and enable activity in the food chain depends on the soil properties, vegetation characteristics and geochemical activity of radionuclides. As well, depends on the "optimal" combination of these factors. Their content in foods can vary by hundreds or thousands of times.

In this regard, the question of studying their degree of involvement in cycles of biogeochemical circulation of the matters is one of the topical issues of radiation ecology of soil and vegetation cover.

The study area or object was soil and vegetation covers of the lower reaches of the Ili river, which occupies the southwestern undrained part of the Balkhash basin. The combination of desert regime and high humidity created an exceptional contrast and diversity of soil and vegetation covers in downstream.

Selection of the region based on the fact that it is the most heavily exposed region within the Ili-Balkhash basin to the anthropogenic influence. The lower reaches of the rivers are the final side of geochemical flow, and natural systems are ecologically very vulnerable.

Accumulation coefficients of radionuclides were calculated in order to assess the cumulative capacity of the main types of vegetation of the lower reaches of the Ili river. Accumulation coefficients are expressed by the ratio of radionuclide contents per unit mass of dry plants to their content in the soil.

Results of the analysis values of the accumulation coefficients indicate the presence of significant differences between radionuclides and between plants. Almost all the studied plants largely accumulate ^{90}Sr than ^{137}Cs. In most cases, the accumulation coefficients of ^{90}Sr higher than KH ^{137}Cs.

Degree of involvement of the studied radionuclides in small biological circulation depends on the specific features of plant, the soil conditions, and the properties of the radionuclides.

^{90}Sr and ^{137}Cs are differentiated by a low level of participation in small biological circulation.

The data on the content of radionuclides in the soil, plants and accumulation coefficients can be used for evaluation of the radio-ecological situation in downstream of the Ile river and forecasting calculations.

P03

The synthesis and physico-chemical characteristics of superabsorbent polymer hydrogels

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Superabsorbent polymer hydrogels can swell to absorb huge volumes of water or aqueous solutions. This property has led to many practical applications of these new materials, in particular, in agriculture for improving water retention of soils and the water supply of plants. The abstract presents the results of the synthesis, study physical and chemical properties of hydrogels on the base from the production of wastes fiber "Nitron" (Polyacrylonitrile), K-30 and salts of 3-d transition metals, swelling polymer hydrogels complex HG-Al and HG-Cr were synthesized, and based on of 37% formalin hydrogel HG-F was made. For assessment application prospects of hydrogels as soil moisture absorber are important energy characteristics of state moisture. The developed hydrogels HG-Al, HG and HG-Cr have been tested for water holding capacity of sand. To estimate, experiments were done by methods of Richards membrane press and by Dolgov capillarimeter. It was confirmed by data from method of determining the wilting point by vegetative thumbnails. In entering process in a dose 0,1% of swelling polymeric hydrogel into sand with culture of barley difference between wilting point in comparison with the control was negligible. It means, moisture which contained in hydrogel to the same extent is involved in moisture availability for plant growth, as well as a capillary.

P04

Sulfur compounds of Kazakh oils and their removal by ionic liquids

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The increase of hydrocarbon feedstock consumption causes problems related to component composition and heteroatomic compounds contained in oil feedstock. The traits of sulfur-containing compounds and their presence in almost all oil fractions define their negative influence on physical and chemical, operational properties of feedstock, cause corrosion attack of equipment and pollution of environmental objects.

Unequal content of hydrocarbon and heteroatomic compounds are peculiarly for hydrocarbon feedstock of Kazakhstan fields. Hydrocarbon classes of oil and oil fractions are represented by alkanes, cycloalkanes, unsaturated hydrocarbons, arenes and their isomeric forms [1]. Sulfur-containing heteroatomic compounds are found mainly in the following forms: hydrogen sulfide and elemental sulfur originated within destructive processes of hydrocarbons; mercaptans and thiols possessing acidic properties and corrosion activity; thermally unstable and neutral at low temperature aliphatic sulfides; thermally stable monocyclic, polycyclic sulfides; heterorganic compounds containing simultaneously sulfur, nitrogen, oxygen and organometallic compounds.

The composition of Kazakhstan oil is mainly represented by light heteroatomic compounds. The analysis of middle and heavy oils of Kazakhstan data was made for establishment of certain classification, systematization of sulfur content and relation of physical and chemical properties. The data related to total sulfur content, density of oil with consideration of depth of occurrence of 53 oil fields, which are in operation was analyzed. To determine regular relationship of physical and chemical properties of these fields their change with increase of sulfur content was established.

The development of new methods of purification and concentration of sulphurous compounds in oil is part of investigation of their composition, structure and properties. Therefore, an important issue is to create effective integrated method of determination and separation of sulfur-containing compounds from oil and its any fractions that allows to go to their detailed study.

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P05

Mesoporous silica functionalized by bio-sourced ligands for the heavy metals removal from wastewater: effect of the morphological characteristics of the solids on sorption properties

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Surface functionalized mesoporous silicas with different morphologies were prepared, followed by the testing of their ability to remove heavy metals from aqueous solutions. Modifications include bio-sourced ligand attachment by grafting to the solid surface whilst the metals tested were essentially Cd^{2+}, Hg^{2+} and Pb^{2+}. Different morphologies have been synthesized including rods, spheres, sheets and platelets and a bio-sourced ligand containing thiol function, glutathione, was then grafted to provide the required group for selective heavy metal removal from wastewater. The effect of the morphology as well as the particle size on the grafting and the adsorption properties (sorption isotherms, uptake kinetics, cycles adsorption/desorption…) was then investigated.

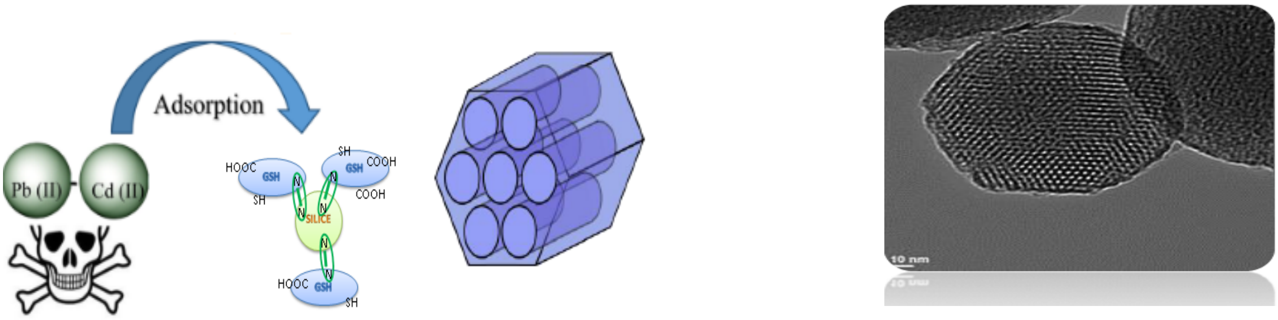

Figure 1. Scheme of the developed material and TEM image of the ordered hexagonal pores of mesoporous silica

The morphological characteristics of the synthesized materials was carried out using Small Angle X-Ray Scattering (SAXS) and electron microscopies (SEM and TEM) , whereas Fourier Transformed Infra-Red Spectrometry (FTIR) and Solid State Nuclear Magnetic Resonance (SSNMR) were used to have a better understanding of the grafting and complexation mechanisms. Metal concentration before and after contact with the solids are determined using Induced Coupled Plasma Atomic Emission Spectromety (ICP-AES). The ligand was successfully grafted inside the porous structures and the synthesized materials prove to be effective for the removal of Cd^{2+} with a rapid metal uptake. These results are encouraging for application in water treatment.

Acknowledgement - The authors would like to thank the Initiatives d'Excellence (IdEx – Interdisciplinaire, Emergence) project from Université de Strasbourg for the financial supporting.

P06

Assessing the biotransformation of hexachlorocyclohexane-isomers by compound-specific isotope analysis

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Hexachlorocyclohexane (HCH) was extensively used as an insecticide in the past. Due to their persistence, HCHs still represent important environmental pollutants. Because specialized microbes are capable of using the different HCH isomers as carbon and energy source, natural attenuation is considered one important option for the remediation of contaminated sites. However, monitoring the extent of HCH biodegradation is challenging due the slow reaction and multiple, isomer-specific reaction pathways. Because this information is difficult to obtain from concentration dynamics, compound-specific isotope analysis (CSIA) is currently explored as a new tool to evaluate remediation efforts based on changes of the isotope ratios of the residual contaminant. The goal of our work was to evaluate the applicability of CSIA for tracking HCH biodegradation by delineating the enzyme and isomer specificity of the kinetic isotope effects responsible for a possible isotope fractionation of HCH.

To this end, we investigated the isotope enrichment factors and apparent kinetic isotope effects (AKIEs) associated with the initial biotransformation steps of the four major HCH isomers (α, β, γ, δ). We performed batch experiments with purified LinA and LinB enzymes that catalyze dehydrochlorination and subsitution reactions of HCHs to pentachlorocyclohexen and pentachlorocyclohexanol, respectively.

We observed large carbon and hydrogen isotope enrichment factors of up to -11‰ and -193‰, respectively. The dehydrochlorination reactions catalyzed by LinA resulted in large ^{13}C-AKIEs independent of the chosen substrates (LinA2 γ-HCH: 1.025 ± 0.001, LinA2 δ-HCH: 1.029 ± 0.001) and enzyme variant (LinA1 γ-HCH: 1.024 ± 0.001). Similarly, ^{2}H-AKIEs did not display enzyme-specific values (LinA1 γ-HCH: 2.4 ± 0.1, LinA2 γ-HCH: 2.6 ± 0.1), whereas substrate-specifity was significant (LinA2 δ-HCH: 4.2 ± 0.1). Current results with LinB and δ-HCH show that the substitution reaction exhibits even larger ^{13}C-AKIEs of up to 1.074.

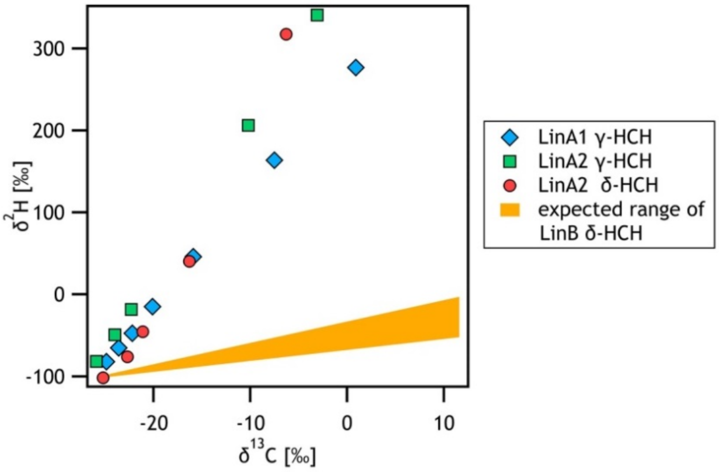

Figure 27: Two dimensional isotope fractionation trends (δ^{2}H vs δ^{13}C) for dehydrochlorination of γ-HCH catalyzed by LinA1 and of γ- and δ-HCH catalyzed by LinA2. Trendlines for the substition pathway were derived from measured C isotope data for δ-HCH transformation catalyzed by LinB and literature data [1].

The substrate specific differences in the ^{2}H-AKIEs suggest subtle variations in enzyme mechanisms responsible for the dehydrochlorination reaction. The simultaneous evaluation of ^{13}C and ^{2}H isotope fractionation, on the other hand, is suitable for differentiation between dehydrochlorination and substitution pathway (Figure 1). Our study reveals the substantial C and H isotope fractionation associated with enzymatic HCH transformations and suggests that CSIA may be suited to monitor biodegradation on the field scale.

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P07

In Situ infrared spectroscopy to characterize surface complexes: optimizing the polarizing mode

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Understanding and predicting the environmental impact of chemical compounds needs to determine their sorption mechanisms and their surface speciation. In this purpose, Fourier Transform InfraRed (FTIR) spectroscopy is one of the most used analytical techniques for the identification and study of molecules and solids [1] because of the straightforward use and interpretation of data. Attenuated Total Reflectance (ATR) phenomenon is very useful in FTIR spectroscopy because it is enabling to study aqueous solutions and aqueous interfaces with iron (oxy)hydroxides colloids. After the preparation of a thin particle film from a colloid suspension, it is possible to follow the interactions between dissolved species and the solid surface, affording chemical insights into the surface chemistry of liquid-solid interface [2].

We have previously used the system lepidocrocite (γ-FeOOH) / (poly)oxometallate ions (Mo(VI)) to illustrate the possibilities of in situ ATR-IR spectroscopy. We are developing new procedures to bring more accurate molecular information, for example at the scale of the faces of the particles, rather than for the particle as a whole. This approach is based on the use of a polarized infrared beam and an anisotropic substrate [3]. To optimize this technique, we have monitored the drying of the colloidal deposit until the thin film stage. We have used polarized in situ ATR-IR to study the dynamic of the organization of the particles during the thin film formation of anisotropic particles of γ-FeOOH.

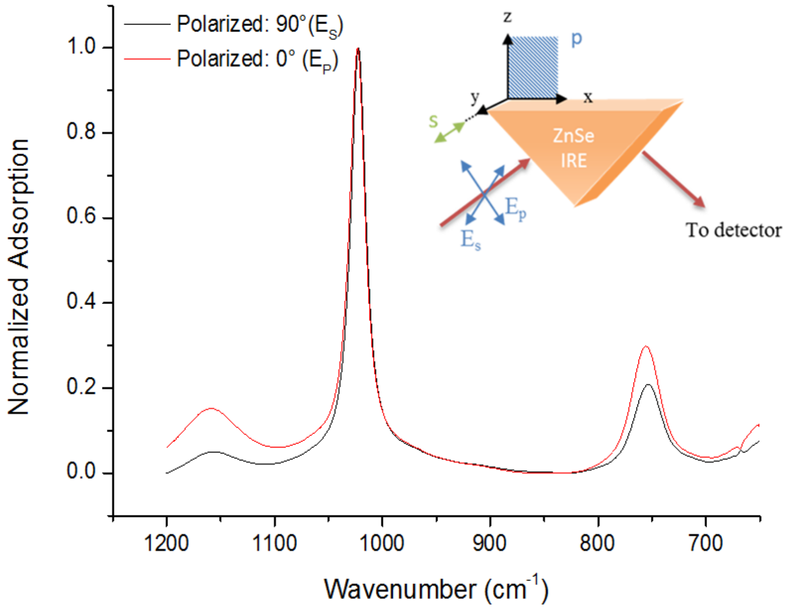

Figure 1 : Polarized infrared spectra of a lepidocrocite thin film: bands of the bending vibrations of the hydroxyl groups of the γ-FeOOH.

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Functionalized Halloysite for enhanced removal of toxic metal ions from aqueous solutions

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During the last years several nanomaterials have been extensively used in the heavy metal ions removal from aqueous solutions. Among them, clay minerals have gathered particular interest owing to their unique features (e.g., high specific surface area, low toxicity and natural availability at low price) [1,2]. Halloysite nanotubes (Hal) are particular clay minerals with a predominantly hollow tubular structure [3,4].

In this work Hal and their derivatives, Hal-NH_2 (see a schematic representation of the synthesis in Figure 1) and Hal-SH, were used as adsorbent materials of lead(II) and mercury(II) ions from aqueous solutions. The adsorption ability of clay nanomaterials towards toxic metal ions has been studied takeing into account important variables of the metal ion solution (e.g., ionic medium, ionic strength, pH, etc.). The Kinetic and the thermodyamic of the metal adsorption were evaluated by using the Differential Pulse Anodic Stripping Voltammetry (DP-ASV) and the Inductively coupled plasma – optical emission specrtoscopy techniques to check the metal ion concentration in the solutions.

Several equilibrium and kinetic equations were used to fit the experimental data. The speciation of metal ion solutions together with the characterization of the adsorbents were considered in order to establish the mechanism of metal ion removal.

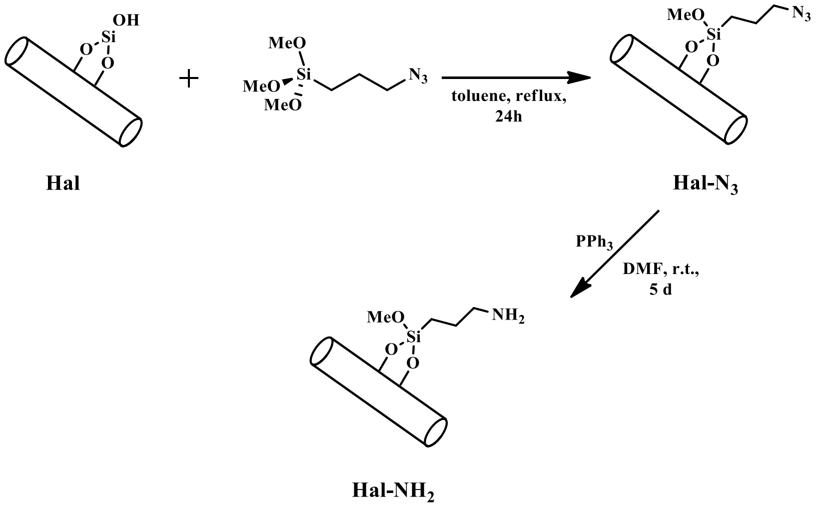

Figure 28: Schematic representation of the synthesis of Hal-NH_2 nanomaterial.

The collected data showed that the functionalization enhances the adsorption ability of Halloysite and makes the nanoclay mineral a good candidate as adsorbent of toxic metal ion from aqueous solutions.

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P09

Bio-char from dead *Posidonia oceanica* residues as adsorbent towards toxic metal ions

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Recently, the pyrolysis of biomass from different algal species and from the Mediterranean sea plant *Posidonia oceanica* have been proposed for renewable fuel production with a maximum oil yield of 54.97% at 500°C, and high heating values of 24-32 MJ kg^{-1}[1,2]. The pyrolysis produces a large amount of bio-char and the accumulation of this byproduct may cause solid waste pollution problems.
Although the composition and properties of bio-char depend on the raw material and on the carbonization process, it is on average composed of amorphous carbon with a highly functionalized surface, which makes it reactive towards inorganic and organic compounds [3].
Considering the reactivity of bio-char, this pyrolysis by-product could be converted in a high value added material by using it as adsorbent towards toxic metal ions and other organic and inorganic pollutants in decontamination processes.
In this context, the bio-char coming from the pyrolysis of local waste biomass (the dead *Posidonia oceanica* residues) was chemically activated and investigated for potential use as adsorbent of toxic metal ions.
The activated and non activated bio-chars were characterized by using different techniques. Then, their adsorption ability towards several toxic metal ions was studied carrying out several experiments with metal ions solutions at pH = 5, containing $NaNO_3$ or NaCl backgrounds, at different ionic strengths and temperatures.

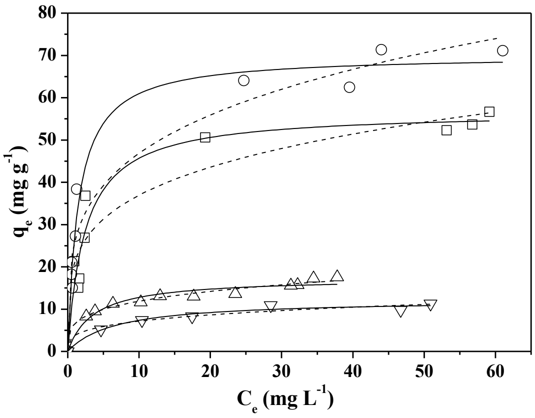

Figure 29: Adsorption isotherms of Pb^{2+} on bio-char from aqueous solutions at pH = 5 containing $NaNO_3$ 0.10 mol L^{-1}, at 10 (▽),25 (△), 40 (□) and 60 (○) °C. Experimental data fitted with Freundlich (dashed lines) and Langmuir (continuous lines) models.

The residual metal concentration in aqueous solutions during the equilibrium experiments was measured by Differential Pulse Anodic Stripping Voltammetry (DP-ASV) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) techniques. Langmuir and Freundlich isotherm equations were used to fit the experimental data (see Figure 1).

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Temporal and spatial surveys of polybromodiphenyl ethers (PBDEs) contamination in soil near a PBDE- utilizing factory in Northern Taiwan

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PBDEs (polybrominated diphenyl ethers) are commonly used flame retardants in the world but they have been recently found to be toxic to organisms, causing thyroid homeostasis disruption, neurodevelopmental deficits, reproductive changes, and even cancer. Decabrominated diphenyl ether (DBDE) is the most commercially used PBDE. However, the monitoring of the dispersion of DBDE spatially and temporally from its utilizing factory in Taiwan remains scarce. A contaminated site near the factory located in Northern Taiwan produced electronic devices that utilized DBDE was identified based on a vegetable PBDE monitoring project in 2013 by Taiwan government. It has been followed up sequential soil surveys spatial and temporal in that contaminated site. The contamination ingredients in soils from 2013 to 2018 were close to the commercial product ones, which suggests the source of contamination was from the factory possible through its air venting hole. The average concentration of DBDE in the main contaminated soil was 615 ng/g soil in 2015, slightly decreased to 604 ng/g soil in 2016, and then increased to 844 ng/g soil in 2017. Through the temporal monitoring, the low degradation rate was found. The contamination of peripheral sites included one site was around 5 μg/g soil which was higher than the others around the main contaminated farm and even in the contaminated site show a serious pollution. It may be possibly caused by an DBDE accidentally dumping or air pollution from the DBDE-utilizing factory. The concentrations of PBDEs in different soil depths were also monitored. The results showed that depth 2-15 cm accounted for the most PBDEs accumulation, indicating the DBDE pollution has been for a while and its transport into deep soil through rainfall. The PBDEs contamination can be uptaken by crops shown in our previous studies and then can be consumed by human, therefore, the continuous monitoring of PBDEs in this site is important and the feasible treatments also should be established urgently.

P11

Surface interactions of Tetrabromobisphenol A, Bisphenol A, and Phenol with Graphene based materials in water: Reaction mechanism and thermodynamic effects

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Graphene-based materials have drawn wide attention in the recent years for novel materials for various environmental applications. Graphene oxide (GO) and reduced graphene oxide (rGO) contain a variety of oxygen carrying functional groups that are chemically reactive. In this study, graphene oxide (GO) and reduced graphene oxide (rGO) were self-synthesized via the modified Hummers method, and their performance was investigated systematically for their removal behaviour of phenol, bisphenol A (BPA) and tetrabromobisphenol A (TBBPA) from aqueous solution. The surface properties and reaction mechanisms of graphene materials are important to be studied for the potential environmental application. rGO showed a slightly higher affinity to phenol, BPA and TBBPA than GO due to major driving forces that include the hydrogen bonding, π- π interactions and higher specific surface area. Adsorption kinetics and isotherms can be well delineated using pseudo-second-order and Langmuir equations, respectively. With the temperature increased, the adsorption of the selected organic contaminants on these graphene materials increased. The positive value of ΔH indicated the endothermic nature. The negative value of ΔG indicated the spontaneous reaction of phenol, BPA and TBBPA on graphene materials. Utilization of rGO and GO is also recognised as a potential approach for debromination of TBBPA. These findings indicate that both rGO and GO is a promising treatment agent, for the removal of phenol, BPA and TBBPA from aqueous solution. Due to this excellent removal performance, rGO and GO can be of great significance for remediation of emerging chemicals from the environment.

Strength of Na-Montmorillonite flocs studied in laminar flow

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Strength of flocs suspended in natural and engineered system can be regarded as a critical factor when we considered the transportation of contaminants. Montmorillonite is a clay mineral with large surface area and high charge density that can be regarded as a large potential for the adsorption of pollutants. Many studies has been reported on the rheological properties of montmorillonite suspension. It is well known that flocculation of montnorillonite suspension can be easily induced when the electrolyte concentration is above Critical Coagulation Conentration (CCC) [1]. Our previous study clarified that the strength of montmorillonite floc continuously increases with an increase of ionic strength above CCC [2]. In the present study, we visualized the flowing behavior of montmorillonite flocs and measured the size of flocs as a function of shear rate in a laminar flow generated by the couette chamber.

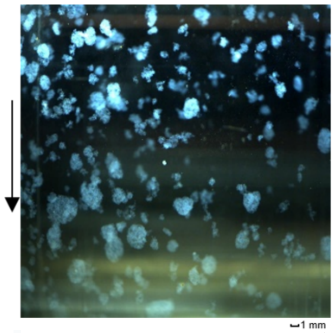

Figure 30: A snapshot of moving flocs （5s^{-1},NaCl 3M）

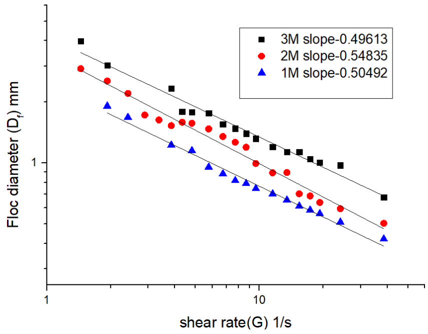

Figure 2: D_f VS G in logarithmic coordinates

Our previous investigation on the PSL model flocs reviewed that the strength of floc is determined by the product of the number of contact bonds, ***Nc***, times the cohesive force of each bonds, ***f*** [3]. Then, the breakup of a floc occurs when the hydrodynamic force acting on the floc exceeds the strength of floc. If the strength of floc can be assumed to be a constant value which is balanced by the shear force exerting on the floc, the following equation, which to predict the size of floc in a certain shear field can be derived:

$$D_f = C\,(\mu\, G / f\, Nc)^{-1/2} \qquad (1)$$

where D_f,C, μ ,G are diameter of flocs, a constant,viscosity and shear rate respectively.

Flocs were made out of Montmorillonite powder (Kunipia-F) in the solution of NaCl with sufficiently high concentration. The detail of preparation process can be referred elsewhere [4]. The suspension of montmorillonite flocs was poured into the chamber of Couette device. The inner cylinder is fixed and outer one rotated clockwise. And the rotating chamber was illuminated by a sheet LED light source. A snapshot of moving flocs was shown in Figure 1.

The maximum distance in the projection of flocs was adopted as the diameter of flocs (D_f). The value at cumulative frequency of 50% (D50) was plotted against shear rate (G) in Figure 2. As indicated in this figure, it was confirmed that the size decreased with an increase in shear rate. The relation qualitatively confirmed the prediction on the basis of Eq.(1). Moreover, higher concentration of NaCl was found to result in stronger strength.

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P13

Activated carbons from Baobab and Balanites shells for diazinon removal: characterization and kinetics studies

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Many groundwater wells are polluted by pesticides in West Africa. The adsorption by activated carbon can be a cheap and efficient method to purify the groundwater in order to allow its consummation as drinking water. In this work, Baobab and Balanites shells have been used to achieve an environmental-friendly pathway for the production of powder activated carbons. These materials have been tested for the removal of diazinon (an organophosphate insecticide) and its hydrolysis product (2-isopropyl-6-methyl-4-pyridinol).

The activated carbons were prepared from dried Baobab (Adansonia digitata) shell seeds and Balanites (Balanites aegyptiaca) shell stones crushed and sieved at 0.8-1.6 mm. The biopolymer contents of each precursor have been analysed chemically and by thermogravimetric analysis (TGA).
The biomass precursors were soaked in KOH solution at impregnation ratio in the range 10%-30%. After evaporation of the solution the dried impregnated materials were pyrolised in the range 700-870°C under N_2 flow. After pyrolisis, the activated carbons have been washed extensively with distilled water in a Soxlet extractor at 100°C to remove the residual KOH until the measured pH of the washing solution was constant. The activated carbons have been characterized for their surface chemistry and their porous structure by elemental analysis and infrared spectroscopy, TGA and nitrogen adsorption-desorption at 77 K. Varying the activation parameters such as KOH impregnation ratio, temperature ramp, and heat treatment temperature, has increased the BET surface areas of the produced carbon from 692 m^2/g to 1249 m^2/g for Baobab biomass and from 863 m^2/g to 1209 m^2/g for Balanites ones. The prepared activated carbons are mainly microporous (pore size lower than 2 nm).

Batch removal kinetics of diazinon pesticide and its main hydrolisis degradation product 2-isopryl-6-methyl-4-pyrimidinol (IMP) has been studied at 2 ppm and 20 ppm initial concentrations on the KOH activated prepared carbons having the highest BET surface areas and a microporous/mesoporous commercial one (S_{BET} = 794 m^2/g, Sigma Aldrich ref. 292591, 4-14 mesh) in tap water (1L, 20 mg of adsorbent). Diazinon has undergone an hydrolisis giving IMP, thus the hydrolisis kinetics of diazinon has also been studied.
The diazinon removal is due both to adsorption and hydrolisis which leads to the formation of IMP. The adsorption is quick and operates mainly in the first hour; wheras after one hour the hydrolysis appears to be dominant. At 20 ppm concentration, 511 mg/g uptake was achieved by using the activated carbon from Baobab(1249 m^2/g) instead of 287 mg/g for the commercial one.

P14

Coupling ultrasound treatment and adsorption on activated carbon for the removal of Carbamazepin

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An efficient method to remove the micropollutants released at the exhaust of wastewater treatment plants is the adsorption on activated carbons. But this adsorption is limited by the slow kinetics of adsorption in non-powdered activated carbon such as granulated or fabric owing to the long diffusion in the porous network taking few days to reach equilibrium [1]. The effect of ultrasound irradiation on the adsorption kinetics of carbamazepine was studied with the aim of accelerating its kinetics of adsorption.

Three activated carbons having various textures were tested as adsorbents: an powder activated carbon prepared in our lab by phosphoric activation of apricot stone (particle size < 71 mm), a granulated one (cylindrical pellets from China) and an activated carbon fabric (KIP1200, Dacarb, France).. The fabric is formed of wowen strand made of three threads, composed of microporous fibre bundles. All the activated carbons were characterized by N_2 adsorption-desorption at 77 K, CO_2 adsorption at 273 K, and density measurement by pycnometry. The fabric was characterized by SEM and mercury porosimetry. The carbon fabric (S_{BET}: 1560 m^2/g, V_{pore}: 0.54 cm^3/g) and the granulated one (S_{BET}: 1044 m^2/g, V_{pore}: 0.35 cm^3/g) are mainly microporous while the powder activated carbon is both microporous and mesoporous (S_{BET}: 1495 m^2/g, V_{pore}: 0.83 cm^3/g).

The adsorption kinetics or degradation of carbamazepin at an initial concentration of 20 ppm were studied at 25 °C in buffered phosphate solution either in silent conditions under orbital stirring (20 mg of adsorbent in 1 L agitated at 250 rpm for 6h) or coupled with ultrasonic treatment in a bath (Eumax, UD80SH-1.3L) at 40 kHz and 12 W acoustic power. The fabric or the granulated activated carbons were only slightly damaged after 6h of sonication yielding to powder formation (less than 14 weight %).The adsorption kinetics have been simulated by a model of volume diffusion allowing to determine the values of the external mass transfer coefficient and the volume diffusion coefficient.

The removal of carbamazepine by coupling of ultrasound treatment and adsorption shows the superimposition of degradation and adsorption. The adsorption kinetics for each adsorbent can be calculated by substrating the degradation from the total removal kinetics of carbamazepin. The adsorption in the ultrasound bath is similar to the one obtained in silent condition through orbital agitation for the powder activated carbon (C/C_0=0.78 after 6h).The adsorption on the powder is quick and the equilibrium is attained in less than 50 min due to the absence of diffusion limitation.

For the fabric and the granulated activated carbons, the irradiation in the ultrasound bath yields to an important acceleration of the adsorption kinetics (C/C_0=0.78 after 6h) with respect to the one obtained through orbital agitation (C/C_0=0.9 after 6h). This is explained by a faster diffusion of the molecules under ultrasound irradiation and confirmed by the simulation using a diffusion model. The ultrasound irradiation allows speeding the diffusion through the macroporous network of the activated carbon fabric and through the porous network of the granulated activated carbon. As a result, the adsorption can be successfully accelerated by using ultrasonic irradiation for these two adsorbent where the porosity usually limits the diffusion.

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P15

Chitosan gels produced by prilling and resulting porous beads

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Chitosan (CS) gel beads were produced by an electromagnetic laminar jet breakup technology also known as “prilling”. The designed pilot has allowed us to form hydrogel beads of milimetric size. By passing an acidic chitosan solution through a calibrated nozzle, a laminar jet is obtained and cut onto spherical and monodispersed droplets by applying vibrations to the nozzle. Then, the droplets are coagulated once they falled in a gelling bath. The obtained hydrogel beads have been lyophilized and stored for a further use as adsorbents for heavy metals adsorption. This equipment allows users to quickly produce sufficient quantities of material for a subsequent industrial scale up. To optimize the process, different parameters (chitosan concentration, acid nature for chitosan dissolution and gelation bath) were varied in order to obtain chitosan beads with various structural and textural properties.

The nature and concentration of the acids used to solubilize chitosan were studied and have shown an impact regarding the chitosan hydrogels’ mechanical strength. Highest strengths have been obtained by using acetic and formic acids. Chitosan concentration (2 to 5 wt. %) has shown a great importance during the prilling process because of its influence on the solution viscosity, which affects the storage modulus of the formed beads. A good agreement was observed between the Newtonian viscosities of the CS solutions and the hydrogels’ storage moduli since their variations were similar. As a result, the internal organisation of the CS chains in the final hydrogels were inherited from the prestine solutions. Gelling bath composition was varied (NaOH, NaOH/EtOH) to obtain high porosities and to ensure a fast gelling in order to avoid the deformation of the beads. After lyophilization, the specific surface areas of the beads have ranged between 12 and 108 $m^2.g^{-1}$ and were highly dependent on the acid used for the solubilization (**Figure 1**). Their internal morphology observed by Scanning Electron Microscopy has shown irregular shaped macropores conferring them variable densities. Their water uptake determined for further use in adsorption processes was found to be dependent on the chitosan concentration and mostly on the nature of the acid used for the solubilisation, and to vary according to the content of residual protonated $–NH_3^+$ groups and of residual conjugated base anion remaining after the extensive distilled water washing following the gelation.

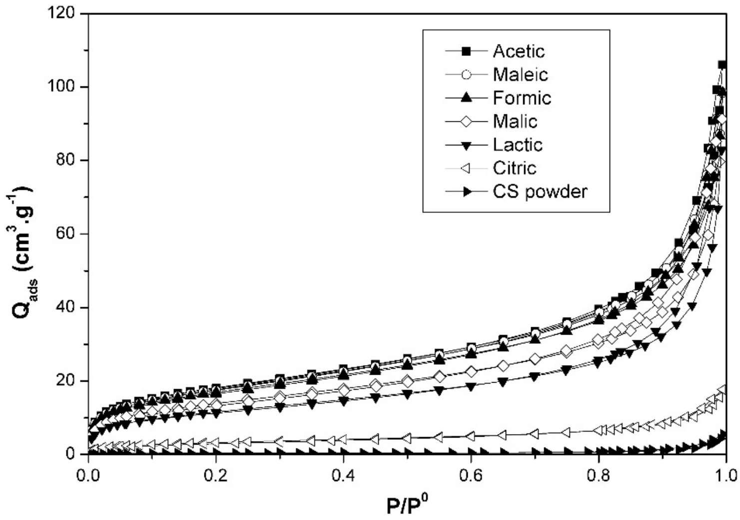

Figure. 1. N_2 adsorption-desorption isotherms of the raw CS powder and “prilled” lyophilized beads prepared from CS 4% (w/w) solutions made with different acids (acetic, formic, malic, lactic, citric and maleic) at 0.5 mol.L^{-1} concentration. Gelation bath was NaOH (10%) aqueous solution.

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P16

Factors for affecting nano bubbles transport in saturated porous media

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An understanding of nano-scale bubble (NB) transport in porous media is important for potential application of NBs in soil/groundwater remediation. It is expected that the physical properties and solution chemistry of NB water highly influences the surface characteristics of NBs and porous media and the interaction between them, thus affecting the transport characteristics of NB. In this study, one-dimensional column transport experiments using glass beads with 0.1 mm size were conducted, where either air- or O_2-NBs water were injected to the column (diameter: 5 cm, height: 10 cm) with different flow rates (Figure 1). The turbidity, pH, EC, DO, and bubble size distribution in the effluent were measured. The bubble size distributions were measured using a resonant mass method. Effects of flow rate, bubble characteristics (gas species and bubble concentration), and solution chemistry (pH and ionic strength) on the NBs transport were investigated based on the column experiments. The results showed that relative turbidities (measured turbidity in the effluents / turbidity in the applied NBs water) during the NBs water injection were higher for NBs water at higher flow rate, indicating the mobility of NBs was enhanced at higher flow rate likely due to an increased drag force against NBs and decreased stagnant region of water flow. In addition, O_2-NBs showed higher relative turbidities as compared to air-NBs. Since zeta potential measurements showed that O_2-NBs are more negatively charged than air-NBs, enhanced repulsive force between O_2-NBs and glass beads might increase the mobility of O_2-NBs. Attachment of NBs was enhanced for NBs water with higher ionic strength and lower pH conditions (Figure 2). The results can be also explained by the effects of solution chemistry on the surface charge of NBs. For NBs water at the same ionic strength, NBs water containing Na^+ showed higher NBs mobility as compared to one containing Ca^{2+}. Physical transport models were tested against the obtained effluent curves of relative turbidities. One-dimensional advection-dispersion equation considering attachment, detachment, and straining terms could well express the obtained curves at different conditions.

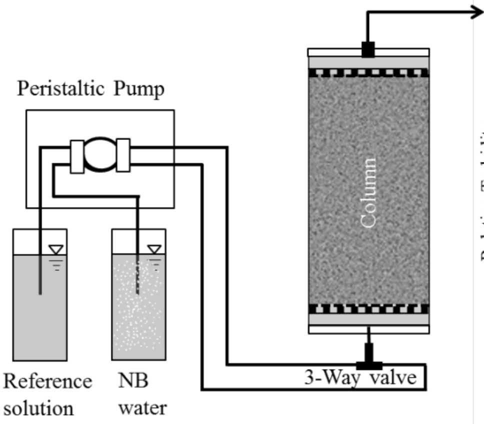

Figure 31: Schematic illustration of experimental setup.

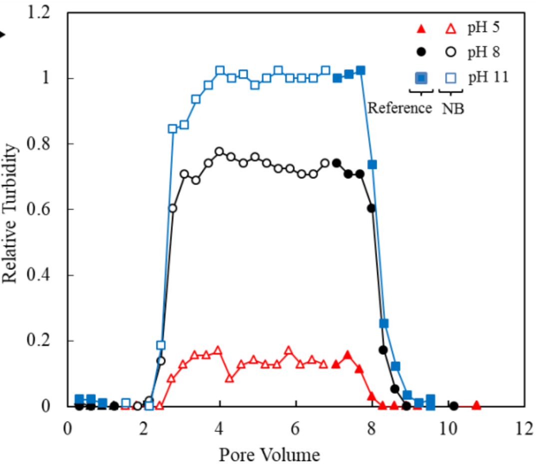

Figure 2: Effluent relative turbidity with pore volume: Effects of pH.

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P17

Effects of dissolved organic matter on transport of cesium in weathered granite soil

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To understand migration of radiocesium (Cs) in soils is an important issue after the accident of Fukushima Dai-ichi nuclear power plant, Japan. Soil organic matters might affect migration of Cs in soils [1]. In particular, dissolved organic matters (DOMs) may alter sorption and transport of Cs in soils. There are two possible processes for DOM-induced Cs transport [2]. First, DOMs in soil solution carry Cs to deeper soil layer. Second, DOMs sorbed on the soil solid surface inhibit Cs fixation, resulting in enhancement of Cs mobility. In this study, we investigated effects of DOM on the Cs transport in a soil by laboratory column experiments.

Soil sample was a weathered granite. It was collected at an abandoned forest in Iitate, Fukushima, Japan. DOM was extracted from a litter from a forest in Chichibu, Saitama. Dissolved organic carbon (DOC) in the DOM extract was 20 mg-C/L. Cs solution was prepared by using a stable CsCl. Cs concentration was 20 mg/L. In addition, Cs-DOM mixed solution was prepared by mixing Cs and DOM solution for 72 hours. An acrylic plastic column having a diameter of 3 cm and a length of 5 cm was used for the transport experiments. The soil column was prepared by packing air dried soil sample up to 3 cm of height. After that, NaCl solution was applied at a constant ponding depth. Sequence of flowing solution were as follows: (i)Cs solution to NaCl solution (pH6, ionic strength of 1 mM), (ii)Cs-DOM mixed solution to NaCl solution and (iii) Cs solution to DOM solution. Cs concentration of the effluent was measured. Some effluent solution was ultrafiltrated to separate water soluble Cs and Cs-organic matter complexes. After the transport experiments, the column was sliced in 1 cm interval and the soil at each section was used to the sequential extraction of Cs [3].

Temporal variation of Cs concentration was almost the same for flowing solution (i) and (iii), while Cs concentration of the effluent using flowing solution (ii) was smaller than the others (Fig.1). It could be expected that DOMs in the flowing solution adsorbed on soil surface and Cs was trapped on the adsorbed DOM. From the results of sequential extraction, exchangeable Cs adsorbed amount of the solution (iii) was smaller than the others (Fig.2). In addition, Cs complexed with DOMs were about 20% in the effluent Cs of DOM solution(solution (iii)). DOMs might remove the exchangeable Cs on soil surface.

In conclusion, DOM didn't facilitate Cs transport. However, there is a possibility that a part of Cs can migrate with DOM.

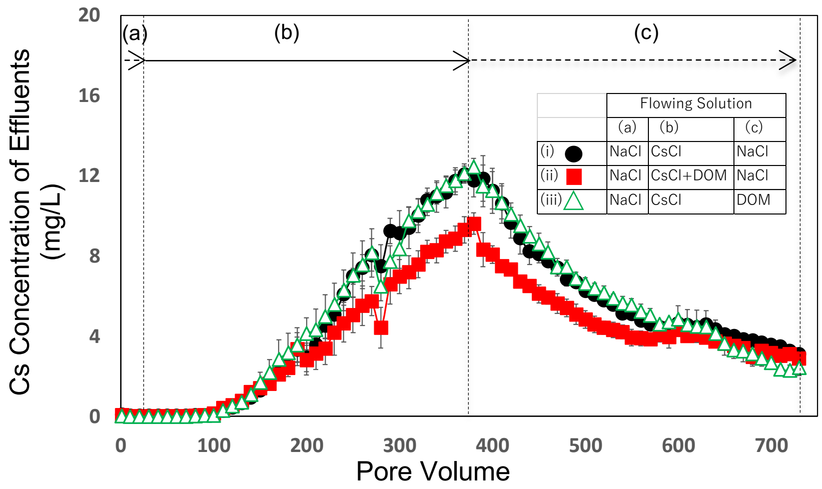

Figure 32: Variation of Effluent Cs concentration

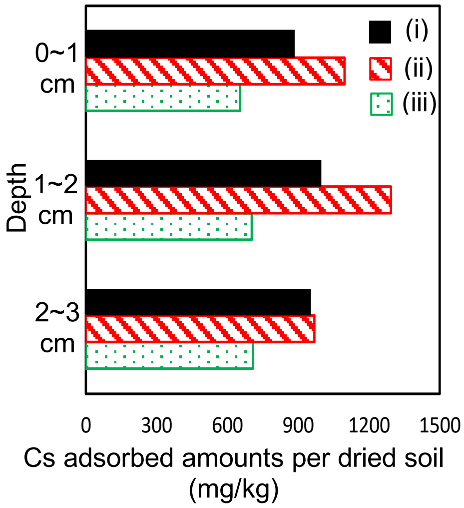

Figure 2: Exchangeable Cs adsorbed amounts by the height

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Environment restoration of abandoned metal mine by using fluidized-bed boiler fly ash

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Fly ash is a by-product of coal combustion in a thermal power plant. Pulverized boiler fly ash is used as a cement substitute in concrete due to pozzolanic reaction. However, fluidized-bed boiler ash is inadequate to be used as a cement substitute in concrete, unlike pulverized boiler fly ash, due to a large amount of free-CaO and $CaSO_4$ generated in desulfurization process, both of which result from differences in combustion method. On the other hand, abandoned metal mines are the source of environmental pollution due to residues after metal mining. Heavy metal ions contained in acid mine drainage from waste metal mines are the most fundamental cause of environmental pollution. In this study, we aimed to restore the environment of waste metal mines. The fluidized-bed boiler ash was used to neutralize acidic effluent discharged from waste metal mines. The immobilization of heavy metal ions contained in the acidic effluent was studied. This study was conducted on an abandoned zinc mine, and fluidized-bed boiler ash from the Korea Southern Power Co., Ltd. was used as fly ash. Figure 1 shows the mine shaft of the abandoned zinc mine, and Table 1 displays the results of the analysis and treatment of the abandoned zinc mine. Based on the results shown in Table 1, a filling experiment was performed on the actual mine shaft of the abandoned metal mine. Figure 1 shows the filling process.

Solution Label	*Pb(ppm)*	*As(ppm)*	*Cd(ppm)*	*Cu(ppm)*	*Zn(ppm)*
Sludges A	*227.53*	*1,380.49*	*65.01*	*299.70*	*7,122.50*
After treatment	*No detect*	*No detect*	*No detect*	*0.041*	*0.453*

Table 1. Heavy metal ions of abandoned mine sludges

Figure 1. Filling of composite fly ash solidifier to abandoned mine

P19

The impact of lipid oxidation on functioning of a lung surfactant model

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Apart from being responsible for sufficient pulmonary compliance and preventing alveolar collapse, lung surfactant (LS) also forms the first barrier for uptake of inhaled pathogens. As such it is susceptible to damage caused by various deleterious compounds present in air, e.g. oxidants capable of oxidizing unsaturated LS lipids. Ground-level ozone can be identified as the main air pollutant responsible for LS lipids oxidation. It causes LS damage already at the concentration of 10-20 ppb. For comparison, a maximum allowable limit of ground-level O_3 concentration established by environmental agencies is equal to 50-75 ppb for 8h daily exposure. And most of the industrialized regions in the world located in warm climatic zones fail to meet this criterion. The reaction of O_3 with POPC follows the well-known Criegee mechanism of ozonolysis. It results in cleavage of the double bond in the unsaturated lipid chain. The main products formed in this process are: the lipid with a shortened and oxidized *sn*-2 chain and the terminal part of the chain, also oxidized. The most probable terminal products are nonanal and nonanoic acid. They readily leave the monolayer by either dissolving to the subphase or evaporation.

This study examines the consequences of oxidizing 20% of unsaturated lipids in an LS model: a mixed 1:1 DPPC:POPC monolayer. POxnoPC (1-palmitoyl-2-(9-oxo-nonanoyl)-*sn*-glycero-3-phosphocholine) is considered as the main oxidation product. Experimental surface pressure-area isotherms are employed to probe changes in the macroscopic properties of unsaturated lipid monolayer induced by oxidation. Microscopic details of the oxidation influence on monolayer's phase behavior are elucidated by molecular dynamics simulations at varying lipid packing. We demonstrate that unsaturated lipids oxidation shifts the isotherm towards larger areas and surface pressures. It also advances monolayer collapse. This is caused by reversal of oxidized *sn*-2 chains of POxnoPC towards the subphase, driven by electrostatic interactions between the aldehyde, glycerin, and water. Increased lipid bulkiness, hindered transition to LC phase, and transfer of oxidized lipids to the subphase have been identified as the most troublesome consequences of this process. They result in reduction of monolayer stability and its capability to withstand high surface pressures. This may lead to uncontrolled and irreversible loss of lipids from the surface.

Reactivity of river materials towards metals – a spectroscopic study

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Suspended matter in rivers (referred to as SPM), are constituted of colloidal and particulate matter, and commonly described as heterogeneous aggregates of mineral, organic and biological phases. Due to their relative small size distribution, their high content in organic matter and amorphous (or poorly crystallized) solid phases, they display a high and reactive surface area. Thus, they play a crucial role in the fate, transport and partition of contaminants in aquatic media, including trace metallic element. Due to their composition complexity, these solids could provide various association modes for metals, determining their mobility and bioavailability and eventually fingerprinting the sources of trace elements. Thus, this study aims to better understand the mechanisms driving the transport of trace element in one given watershed, and by extension the interaction between metallic elements and SPM in aquatic media.

The first part of this work was then dedicated to the study of Zn status in the different SPM samples through the use of XAFS experiments at Zn K-edge in fluorescence mode (SAMBA beamline) as Zn content was shown to vary from 200 to 600 ppm. Although some variations could be noticed on the XAFS oscillations, linear combination fitting of XANES and EXAFS data suggest that Zn is predominantly associated to clay minerals in those SPM. Further fitting of Fourier-filtered k^3*khi(k) signals evidence a variable contribution of Zn-S backscattering to the oscillations, suggesting variable amount of Zn sulfides (from 5 to 15%) in those natural materials, that remain minor Zn carriers.

In order to evaluate the SPM affinity towards trace metallic element, batch sorption experiments were performed with increasing zinc concentrations in solution. Moreover supplementary controlled and simplified particles were also prepared in order to better understand the relation between natural surfaces and Zinc. Indeed, to mimic the mineral fraction of natural SPM, iron-hydroxide coated illites (illite-FeH) were prepared as analogous controlled particles. The association mode of Zn to those natural surfaces was then followed by XAFS at Zn K-edge along adsorption isotherms.

This study confirms the role of clay minerals in Zn behavior and distribution in the water column of river. In the case of Moselle waters, which integrate a relatively large watershed, clay minerals were shown to be the predominant carriers of Zn. Moreover, these XAS experiments confirmed the variation of binding mode of metals onto natural surfaces (including clay minerals and organic matter) with increase of metal concentration in solution.

P21

Ni isotopic fractionation at the interface with mineral phases

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Nickel is thought to have had a crucial role in the early Earth`s [1] as a biologically active trace metal. Nickel isotopes have recently been proposed as a new tool to investigate biogeochemical processes regulating the metal cycle in surface layers. Up to now, however, a complete comprehension of reaction mechanisms responsible for Ni isotopic fractionation factors is still missing [2],[3]. Nevertheless, the use of isotopic tool to unravel biogeochemical cycle of an element needs precise knowledge and characterization of those fractionation mechanisms. In this study, to better constrain the causes of Ni isotopic fractionation, and to associate them to the modification of its chemical status or speciation, the isotopic tool was coupled to X-Ray Absorption Spectroscopy (XAS). Nickel sorption isotherm experiments were conducted on different pure mineral phases, with cation exchange capacity (nontronite) and without (goethite, talc, and cacite). Experiments were performed at constant pH =7 value and variable Ni concentration. Nickel X-ray absorption spectra at Ni K-edge were collected on solid phases in fluorescence mode. Measurements of δ^{60}Ni values were performed both in solution and on solid phases. Obtained results highlighted that, in the case of nontronite, Ni K-edge spectra presents the same spectrum as the one obtained for hydrated Ni in solution, suggesting that Ni is predominantly present on the surface as outer-sphere complexes. The weakness of electrostatic bonds may explain the negligible isotopic fractionation $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ observed for this charged clay mineral.

In the case of mineral phases presenting specific surface sites, where Ni can form inner-sphere complexes, e.g. talc and goethite, a preferential sorption of light isotopes was observed, in agreement with previously published data [3],[4]. For Ni sorption isotherms conducted on talc, $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ was calculated between -0.29 ‰ and -0.86 ‰, but any clear trend was observed as a function of percentage of Ni sorbed. On the contrary, when Ni sorbed on goethite passed from 3 % to 0.5 %, the calculated $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ was -0.43 ± 0.07 ‰ and -0.94 ± 0.07, respectively. Increasing Ni concentration in solution increases Ni competition for goethite specific surface sites, promoting the sorption of light isotopes.

Interestingly, a different behaviour is observed for Ni sorption on calcite. Increasing the amount of Ni sorbed from 3 % to 82 %, $\Delta^{60}\mathrm{Ni}_{\mathrm{sorbed\text{-}dissolved}}$ varied between -0.23 ± 0.07 ‰ and +0.17 ± 0.07 ‰, respectively, with almost no fractionation at about 15 % of Ni sorbed. These results can hardly be explained with only surface sorption processes. It is known that retention of divalent cation on calcite is regulated by both adsorption and precipitation of metal carbonate and hydroxides, depending on metal concentration in solution [5]. The EXAFS Fourier Transform data of Ni-$CaCO_3$ showed, indeed, the presence of a Ni second neighbor (at 3-3.3 Å) that can be attributed to surface precipitation.

These preliminary results suggested that, similarly to goethite, at low % of Ni sorbed, solid phases are enriched in light isotopes, but formation of $Ni(CO_3)_2$ in solution and successive precipitation could contribute to the association of heavy isotopes with the solid phase. However, further investigations are needed to better characterize the interaction of Ni mechanisms at calcite surface.

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Elaboration and characterization of new flat membrane supports from Yagoua clay

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The present work aims the valorization of Cameroonian clay from the Yagoua region to produce macroporous ceramic filters for water treatment. Several analyzes were carried out to characterize the clay powder used for the formulation of the ceramic supports. These include the elementary chemical composition, the specific surface area by nitrogen adsorption – desorption method (BET), and the particle size analysis. These characterizations were supplemented by measurements of X-ray diffraction (XRD), vibrational spectroscopy (IR), thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The elaboration of flat membrane supports involved the formulation of a plastic ceramic paste consisting in a combination of clay powder, water and an organic material, rice husk as a pore former. Several parameters were considered in the formulation of the supports namely, the clay - rice husk ratio in various mixtures (90-10; 80-20; 70-30; 60-40), the drying time of the paste (24h) and the final sintering temperature (900°C, 1000°C, 1100°C and 1200°C). The porous volume, mean pore diameter, surface morphology, mechanical strength, chemical resistance and weight loss after firing ceramic filters were measured. The sintered supports at 1100 °C with a clay-rice husk ratio of 70-30 had a porosity of 43.7% and an average pore diameter of 6.2µm. The mechanical strength obtained for this chosen formulation was 10.4 MPa. The flat ceramic supports processed by roll-pressing and fired at different sintering temperatures (5 cm in diameter and 3 mm in thickness) presented no defect on the surface and were resistant in both acidic and basic media. The ceramic filters obtained are of great interest in the preparation of different microfiltration membranes for water purification.

Keywords: Clay, Rice husk, Ceramic support, Sintering, Microfiltration.

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P23

Formaldehyde remediation from wastewater by self-regenerating bio-clays

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Formaldehyde (FA) is a common organic chemical used in production of resins, adhesives, and preservatives. These processes produce acidic and highly FA concentrated wastewater (3000-10,000 ppm FA, pH 3-4.5). Due to the toxic and carcinogenic nature of FA, these wastewaters need to be properly treated prior to release from the industrial plants. To date, FA remediation technologies fall short and application problems prevent high efficiency. Bioremediation is the most favorable technology because microorganisms can degrade FA completely. However, it is difficult to implement due to bacterial sensitivity to the high FA concentrations and acidity. In the following study, a material was designed to adsorb and bio-degrade FA from wastewater in a one-step, self-regenerating process.

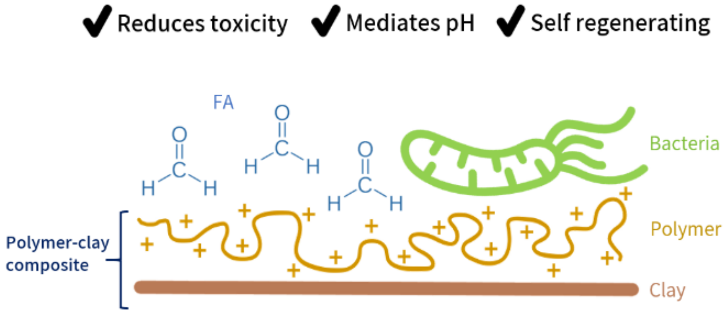

Figure 1: Illustration of formaldehyde remediation by the proposed bio-clay

The composite material is based on three components - montmorillonite clay (MMT), polyethyleneimine (PEI) and a FA degrading *Pseudomonas Putida* (Fig. 1).

Initially a polymer clay composite was designed and characterized. PEI was adsorbed on MMT at high pH values to reach a favorable polymer configuration and maximal adsorption (0.3g polymer/g clay). The resulting composite had an overall positive surface charge and a high concentration of free amine functional groups as seen by zeta potential, FTIR and XRD measurements. FA, as hypothesized, was covalently bound to the MMT-PEI composite, yet the binding was reversible and pH dependant. The binding trends of FA to the composite at pH 8.5 fit the Langmuir model and had a Q_{max} of 81.4 mg/g composite.

Several *Pseudomonas Putida* strains were isolated from agricultural soils. The most robust strain was immobilized on the MMT-PEI composite and characterized in terms of adsorption, SEM and confocal measurements. Finally, efficiency of the complete composite (MMT-PEI-Bacteria) was tested in comparison to free cells in solution. The results showed that the free bacteria in solution were unable to withstand the high FA concentrations and low pH whereas the composite material could degrade continouously many cycles of highly concentrated FA waters. The novel bio-clay exhibited several functionalities which enhanced the biodegradation process: 1. The composite adsorbs FA covalently yet reversibly which reduces toxicity in the vicinity of the bacteria. 2. The composite buffers the wastewater solution and adjusts pH to allow better degradation conditions. 3. The slow release and degradation of FA from the matrix allows regeneration of the matrix and extended long term use.

Therefore, this material is a promising solution to the common drawbacks of FA removal technologies.

Electroanalytical development for indium speciation analysis

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Recent studies have pointed out a growing input of indium element in the environment as a result of its use in the manufacturing of high-technology products. However, the geochemical fate of Indium in natural waters is still poorly understood. Therefore, reliable and easy-handling analytical tools for indium speciation analysis is then required. Voltammetric techniques are pertinent for *in situ* measurements of trace-metal speciation, providing detection with high sensitivity and resolution. In this work [1], we report the possibility to measure the total and free indium concentrations in solution using two complementary electroanalytical techniques, respectively SCP (Stripping Chronopotentiometry) and AGNES (Absence of Gradients and Nernstian Equilibrium Stripping).[2]

Regarding SCP two types of set-ups are tested, opening the possibilities for laboratory studies and field applications. For total metal concentration, an excellent limit of detection (LOD) of 0.5 nM was obtained in the laboratory set-up (Figure 1) while a reasonable LOD of 30 nM for the field set-up. The free metal determination determined using AGNES technique shows satisfactory LOD's up to 1.4 nM on the laboratory set-up.

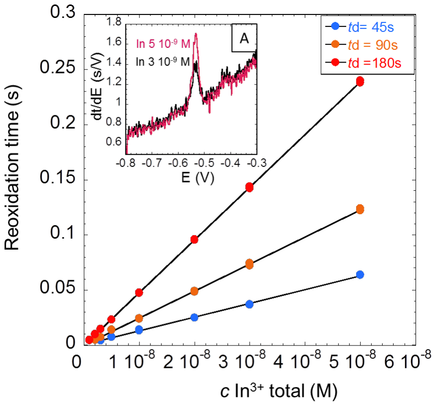

Figure 33: Examples of SCP calibrations for deposition times of 45s, 90s and 180s, obtained in 100 mM NaClO4 medium, pH 2.3. Inset: SCP curves of 3 and 5 10^{-9} M for the deposition time of 180s showing the signal to noise ratio.

Since the interaction of Indium with natural organic matter is expected to be one key for indium speciation in environment, we decided to test AGNES in presence of a well-characterised humic sample,[3] as a representative colloidal phase in freshwaters. We then verified that AGNES was able to provide robust speciation data in experiments in presence of humic matters.

This study demonstrates highly satisfactory sensing performance and robustness of these two techniques. Their main advantages are that they are easy to implement, they exhibit a high sensitivity (nanomolar detection) together with good result reproducibility.The complementarity of these two analytical tools will be benefit for the further in-depth thermodynamic analysis of the Indium binding with molecular or colloidal ligands. The development of electroanalytical techniques dedicated for indium speciation would also open new routes for using Indium as a potential tracer for biogeochemical processes of trivalent elements in aquifers.

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P25

Turbulent hetero-aggregation of unequal-sized particles: Size ratio effects

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The co-existence of different types of colloidal particles causes the aggregation between different particles called hetero-aggregation. Moreover, colloidal particles are usually subjected to flow fields in water environments. In this study, therefore, we have analyzed the experimental results of the turbulent hetero-aggregation with the theoretical calculation for a simple shear and an axisymmetric extensional flows. The hetero-aggregation experiments for unequal-sized latex particles with three different size ratios were performed. The hetero-aggregation rates were estimeted from the reduction of the number of free smaller particles due to the hetero-aggregation. We have plotted capture efficiencies of hetero-aggregation rates for unequal-size particles against size ratio in Figure 1, where the size ratio is defined as the smaller particle radius divided by the larger one. The symbols are experimental values. The red and black lines are the calculated values by solving the convective-diffusion equation in an extensional flow [1] without and with Brownian diffusion, respectively. The blue line is the ones calculated by the correlation equation based on a hydrodynamic trajectory analysis in a simple shear flow [2]. The experimental capture efficiencies show nearly constant irrespective of size ratio, while the calculated capture efficiency in a simple shear flow considerably slows down with decreasing size ratio. In contrast, the capture efficiency in the extensional flow is less sensitive to the size ratio. Comparing the experiments with these theories, we found that the turbulent hetero-aggregation rates for unequal-sized particles can be more comparable with the calculation in the extensional flow than that in the simple shear flow. This implies that the flow in the microscale of turbulence is approximated as an axisymmetric extensional flow rather than a simple shear flow.

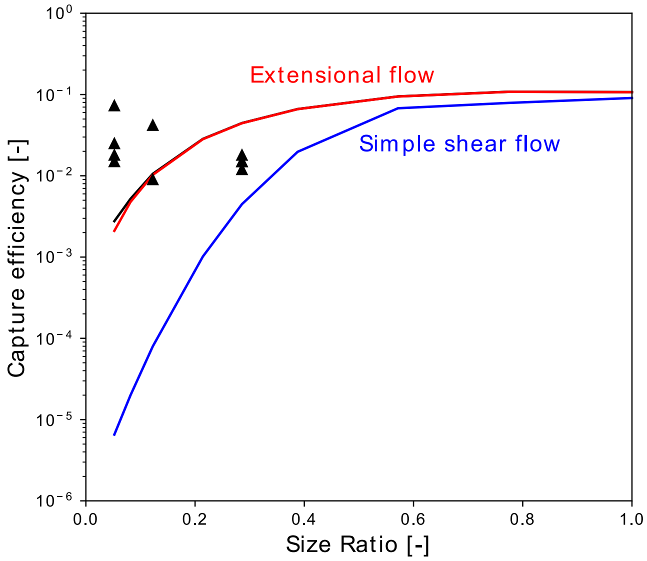

Figure 34: Capture efficiency vs. size ratio for unequal-sized particles, where the size ratio is defined as the smaller particle radius divided by the larger one: The symbols are experimental values. The red and black lines are the calculated values by solving the convective-diffusion equation in an extensional flow [1] without and with Brownian diffusion, respectively. The blue line is the ones calculated by the correlation equation with the hydrodynamic trajectory analysis in a simple shear flow by Han and Lawler [2].

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P26

Effect of Al-substitution on the surface charge characteristics and Pb^{2+} adsorption on Hematite

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Al-substitution in hematite is ubiquitous in soils, and has strong influence on the structure and physicochemical properties of hematite. In this research, Al-substitution hematite was synthesized by coprecipitation method. The obtained samples were denoted as H-0, H-5 and H-10 with different amount of Al-substitution. With the increase of the amount of Al-substitution, it was found that the crystallinity of hematite decreased and the specific surface area (SSA) increased slightly. The scanning electron microscopy (SEM) images and high resolution transmission electron microscopy (HRTEM) images revealed that the morphology of hematite changed from rhombohedral to flakes and the proportion of crystallographic plane (001) increased. The substitution of aluminum promoted the lattice defects of hematite leading to the increase in the content of hydroxyl groups. The relative content of OH$^-$ increased from 22.32% (H-0) to 31.56% (H-10) which was analysed by X-ray photoelectron spectroscopy (XPS). The singly coordinated ($\equiv FeOH^{-0.5}$ and $\equiv AlOH^{-0.5}$) and triply coordianted ($\equiv Fe_3O^{-0.5}$ and $\equiv Al_3O^{-0.5}$) surface sites produced a significant activation on the crystallographic plane (001) which enhanced the surface charge density of hematite(Figure 1). The results of Langmuir fittings of adsorption isotherms showed that the adsorption density of Pb^{2+} on hematite was 3.51umol/m^2 (H-10)>1.23 umol/m^2 (H-5)>0.82umol/m^2 (H-0) at pH 5.0(Figure 2), which is consistent with the XPS results and acid-base titration results. The results of this research are helpful for us to understand the chemical behavior of Al-substitution in soils and the speciation transformation of lead in the environment.

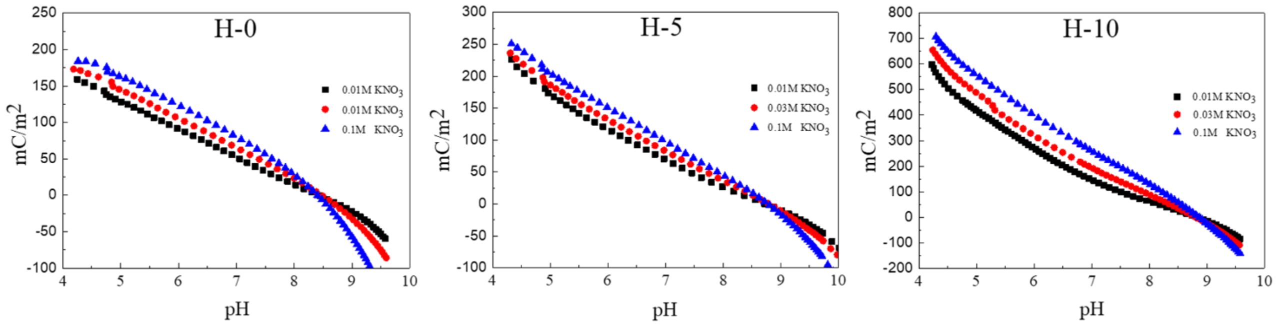

Figure 35: Charged density (mC/m^2) curve of Al-substitution hematite.

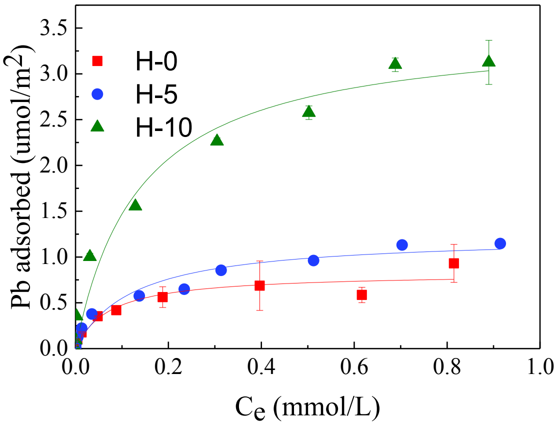

Figure 2: Adsorption isotherms of Pb^{2+} on Al-substitution hematite at 0.01mol/L KNO$_3$ and pH 5.0; solid lines: fitted Langmuir equation.

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P27

Modelling the potential mobility of heavy metals in red soil in Southern China

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The pollution of heavy metals in soil has become a normalcy of soil in China due to sewage irrigation, heavy metal atmospheric sedimentation, pesticide fertilizer use and industrial sludge and municipal solid waste composting and other human producing activities. The bioavailability and toxicity of heavy metals in soil are not only related to the total amount, but more to the species of heavy metals in soil. The Multi-surface model was used to predict the labile heavy metals and their speciations in the soil. The model considered complexation in solution and interactions with soil organic matter (SOM), a clay mineral and hydrous Al, Fe and Mn oxides. The amounts of reactive metals were derived from extraction with 0.43M HNO3, and the concentration of free heavy metals in the soil which was measured by Donnan Membrane Technique (DMT) for testing the accuracy of prediction. The prediction results of the Multi-surface model using default parameters were consistent with the actual measured values of free Zn, Cu and Cd in the soil solution, while the predicted value of free Pb was much different from the measured value. By the model optimization, several heavy metal forms in the red soil were well predicted. The predicting results of Multi-surface model showed that the SOM and crystalline iron oxides in the soil played the important role for adsorbing Zn, Cu and Cd, while the content of manganese oxide in soil had a great influence on the adsorption of Pb. The fraction of reactive metals, which were interacted with dissolved SOM according to the modelling, was predominantly $< 4\%$ for Pb and Cu, $< 0.4\%$ for Zn, and $< 14\%$ for Cd. We suggest further quantitative and qualitative investigations on the Multi-surface model to the soils with high iron content in southern China to improve the prediction of the potential mobility of heavy metals.

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Effect of soil fulvic and humic acid on Pb binding to the goethite/solution interface: LCD modeling and speciation distribution of Pb

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The effect of soil fulvic (JGFA) and humic acid (JGHA) on Pb binding to goethite was studied with the Ligand Charge Distribution (LCD) model and X-ray Absorption Fine Structure (XAFS) analysis. In the LCD modeling, the inner-sphere complex between the –FeOH$^{-0.5}$ of goethite and –COOH of HS and three main types of Pb bound as Pb-goethite (Pb bound to goethite), Pb-HS-goethite (Pb bound to adsorbed HS) and goethite-Pb-HS (Pb bound as bridge between goethite and HS) were considered. The spatial distribution of the small JGFA particles was equal in Stern layer. However part of the large JGHA particles was presented in diffuse layer which was determined by the JGHA diameter and environmental conditions.

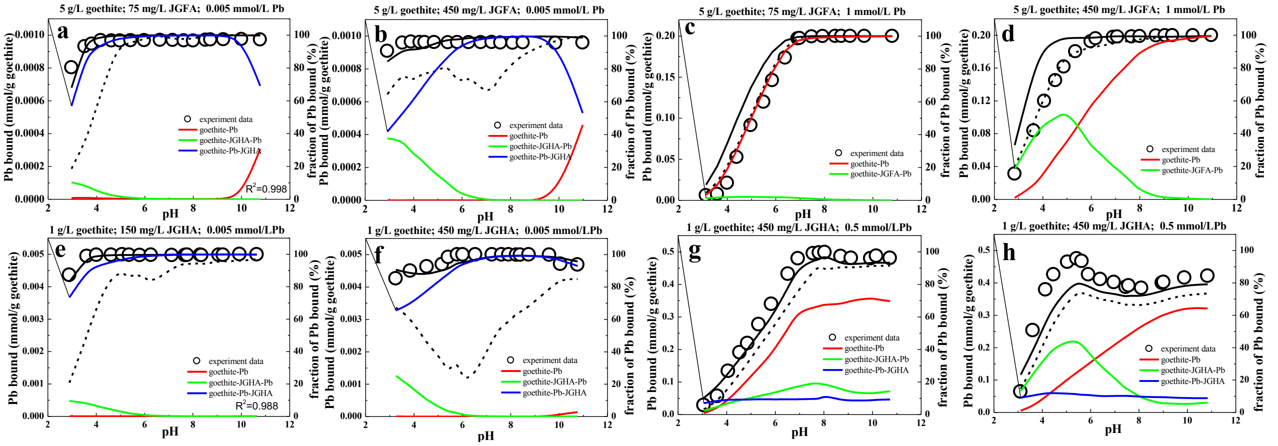

Figure 36: The amount of Pb bound by the goethite-HS complex as a function of pH in the ternary systems in 0.10mol/L KNO_3.

As shown in Figure 1, the results showed that Pb binding to goethite-HS complexes could be described reasonably well with the LCD model and the speciation distribution of Pb was analyzed. At low Pb levels, Pb-bridges were important for both JGFA (Figure 1a, b) and JGHA (Figure 1e, f). At high Pb levels and low HS loading (Figure 1c for JGFA and Figure 1g for JGHA), Pb-goethite almost dominates over the entire pH range; but at high HS loading, the primary species was goethite-HS-Pb at acidic pH and goethite-Pb at alkaline pH. Compared with JGFA (Figure 1d) there was a constant contribution of Pb-bridge about 10% for the JGHA (Figure 1h).

Experiment conditions	LCF analysis of EXAFS		LCD model calculation		
	HS-Pb	Goe-Pb	HS-Pb	Goe-Pb	Goe-Pb-HS
5g/L goethite; 75mg/L JGFA; 1mmol/L Pb	10.5%	89.5%	4.8%	95.2%	0
5g/L goethite; 450mg/L JGFA; 1mmol/L Pb	59.8%	40.2%	58.8%	41.2%	0
1g/L goethite; 150mg/L JGHA; 0.5mmol/L Pb	44.8%	55.2%	24.4%	54.4%	21.2%
1g/L goethite; 450mg/L JGHA; 0.5mmol/L Pb	67.3%	32.7%	57.8%	26.6%	15.6%

Table 1: Pb species at pH5 obtained from the LCF analysis of the EXAFS and LCD model calculation.

The Linear Combination Fit (LCF) results of EXAFS spectra for the ternary systems are presented in Table 1. With the fitting the spectra of the binary systems goethite-Pb and HS-Pb were applied as the reference. The fitting results indicated that with the increased HS loading more Pb was bound to the adsorbed HS and less to goethite, which supported the present LCD calculations.

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P29

Quantification of humic and fulvic acids in mixtures before and after preferential adsorption to minerals

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The adsorption of humic substances (HS) to minerals has attracted the attention of an increasing number of researchers over last decades due to its important role in many soil processes. However, the competitive adsorption between humic acid (HA) and fulvic acid (FA) to minerals is not well understood, partly because of a lack of analytical methodology to effectively separate HA and FA in their mixtures. This study aimed to develop and evaluate methodogies to quantify HA and FA in their mixtures without or after interaction with minerals. Three methodologies were tested, comprising Acid Precipitation, Ultraviolet-Visible (UV-Vis) spectroscopy, and Size Exclusion Chromatography (SEC) with a UV-Vis detector. Overall, the UV-Vis methodology (which combined TOC analysis with UV-Vis measurement) is recommended to quantify HA and FA in their mixtures before (94%±6% recovery for HA and 105%±8% recovery for FA) and after (91%±3% recovery for HA and 113%±12% recovery for FA) adsorption to goethite. The SEC method (which combined TOC analysis with SEC chromatography) is reasonable in measuring HA and FA without adsorption to minerals (88%±13% recovery for HA and 106%±7% recovery for FA). However, the SEC method is not reliable in quantifying HA and FA after adsorption to goethite due to modification of the SEC chromatograms upon the preferential adsorption, especially at low HA fractions (<25%). HA concentration was overestimated with Acid Precipitation method when the relative fraction of HA is low (<50%) with and without the influence of adsorption to goethite. A recovery of more than 100% points to the precipitation of some FA that is, by definition, interpreted as HA in the measurement. With Acid Precipitation, the accuracy for FA estimation has been improved after adsorption, in particular in mixtures with a high fraction of fractionated HA .

All those three methodologies can well estimate HA and FA amount to some extent, and the accuracy in prediction is highly dependent on the composition and structural properties of HA and FA. Preferential adsorption of more aromatic particles modifies properties of HA and FA, and thus affects the performance of those methodologies.

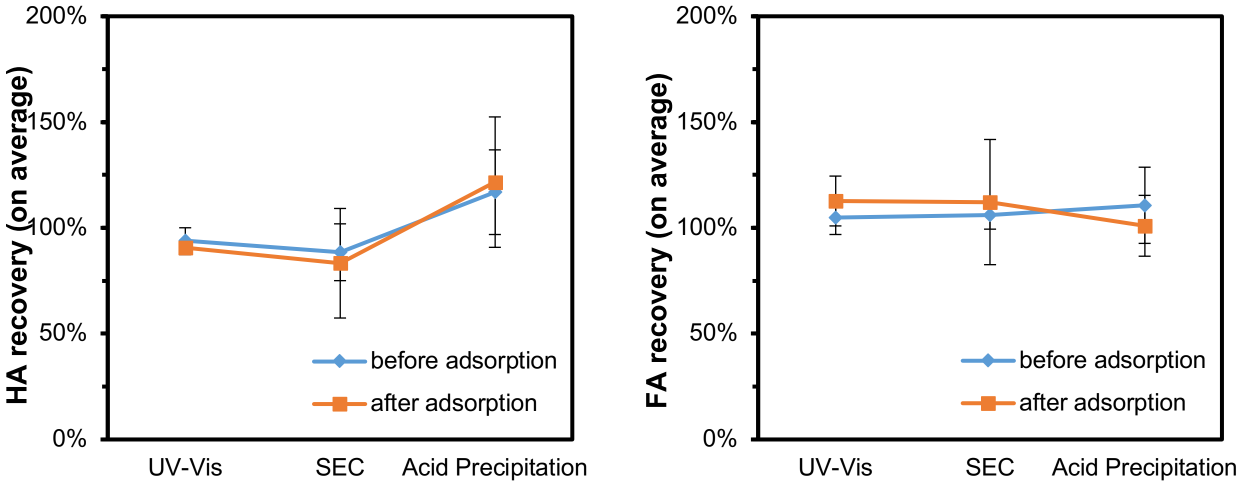

Figure 37: HA and FA recoveries on average over variation of concentrations before and after adsorption with UV-Vis, SEC and Acid Precipitation. It should be noticed that average recovery of HA after adsorption quantified with SEC was calculated only for the mixtures at higher HA fraction (>50%).

P30

Renewable adsorbents originating from the biomass of canola seeds in the removal of Cd^{2+} from water

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Water resources are considered fundamental elements since their multiple use are indispensable for the development of living beings. The concern with the contamination of this natural resource is due to the environmental problems caused by different anthropic activities. In addition to the monitoring of the water quality, it is necessary to search sustainable ways to remediate this environmental compartment. This research aimed to use *in natura* and modified residues of canola seed as adsorbents aiming the removal of Cd^{2+} from water. The canola seeds were obtained from the Hyola 411 genotype and the biosorbent was modified with solutions of H_2O_2, H_2SO_4 e NaOH (0,1 mol L^{-1}), resulting in four adsorbents: C. *in natura*, C. H_2O_2, C. H_2SO_4 and C. NaOH . After the modification of the materials it was realized the characterization of them by MEV, FT-IR, TG/DTG and BET/BJH besides the chemical composition and pH_{PZC}. The possible interaction between pH of the Cd^{2+} solution and the adsorbent mass, besides the kinetic, equilibrium and thermodynamic conditions of adsorption, were evaluated. A significant difference ($p<0,01$) was found for the adsorbent mass, with the highest removal rates for the mass/volume relation of 4 g L^{-1}. The pH range evaluated (3.0 to 7.0) did not influenced the adsorption process, in this sense; these adsorbents could be applied in water with different conditions of pH. It is observed that the adsorption of Cd^{2+} by canola adsorbents is a fast process with a equilibrium time in about 80 minutes. The model of pseudo-second order presented great R^2 as well as good proximity between the estimated ($Q_{eq\ calc.}$) and experimental ($Q_{eq\ exp}$) values suggesting the occurrence of Cd^{2+} chemisorption (Ho & Mckay, 1999). Table 1 presents the results of the equilibrium tests by the mathematical models of Langmuir, Freundlich e Dubinin-Radushkevich (D-R). The adsorption of Cd^{2+} occurs in mono and multilayer as observed by the mathematical adjustments by Langmuir e Freundlich (Table 1).

Table 1. Parameters reffering to the models of Langmuir, Freundlich and D-R to adsorption of Cd^{2+} by adsorbents C. in natura, C. H_2O_2, C. H_2SO_4 e C. NaOH

	---------------- Langmuir ----------------				--------- Freundlich ---------			-------------- D-R --------------		
	Q_m	K_L	R_L	R^2	K_f	n	R^2	Q_d	E	R^2
C. *in natura*	11.587	-3.80E-04	1.082	0.991	4.078	2.963	0.945	3.89E-04	12.700	0.961
C. H_2O_2	10.299	8.38E-03	0.374	0.983	1.938	1.826	0.961	7.18E-04	10.314	0.980
C. H_2SO_4	15.699	1.25E-01	0.038	0.997	92.747	15.699	0.997	4.44E-03	6.402	0.985
C. NaOH	24.155	4.07E-02	0.109	0.996	9.103	4.645	0.992	4.40E-04	14.434	0.983

Q_m and Q_d: maximum capacity of adsorption; K_L: constant related with the forces of interaction adsorbent/adsorbate; R_L: Langmuir constant; R^2: coefficient of determination; K_f: related to adsorption capacity; *n*: related to the heterogeneity of the solid; *E*: medium energy of sorption.

It is important to mention the elevation of 2 times in the maximum capacity of adsorption (Q_m of Langmuir) for the NaOH modified adsorbent and the elevation of twenty-two times for C. H_2SO_4 (K_f of Freundlich). The thermodynamic parameters indicate that in all the studied cases the adsorption of Cd^{2+} is a spontaneous process ($\Delta G < 0$). Due to the values of $\Delta H < 0$ the reactions of adsorption are exothermic releasing energy to the medium. It can be concluded that the modifying solutions contribute in increasing the Cd^{2+} removal capacity. In this sense, the use of these adsorbents presents a renewable alternative for the decontamination of water containing Cd^{2+}, helping the processes of water treatment and consequently the preservation of the environment.

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P31

Oxidation of Acetaminophen by different phases of manganese dioxides

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Manganese dioxide, a common natural mineral composition, siginificantly affects the transformation of aqueous phenolic pollutants. Different phases of manganese oxides shows differences in the catalytic activity for pollutants degradation, which has attracted more attention. Herein, two phases of manganese dioxide δ-MnO_2 and γ-MnO_2 was synthesised and used to oxidate acetaminophen, respectively. In our work, conversion of acetaminophen by δ-MnO_2 was 60% in neutral system, but only 40% was transformed by γ-MnO_2 after 3 h reaction. Lattice strusture influenced the electron trasfer ability of these two MnO_2, leading to a discrepancy in the removal kinetic (pesodu second-order to δ-MnO_2, retardant first-order to γ-MnO_2). Notably, the ratio of Mn(III) against Mn(IV) before and after reaction remained close for each phases of MnO_2, but an excessive binding of Mn(II) species to δ-MnO_2 was observed. Although γ-MnO_2 was less appreciable catalyst in sight of removal efficiency, it was more resistant to co-existing transition metal cations. This finding indicated that the processes of δ-MnO_2 included one interlayer cation exchanging step more than that of γ-MnO_2, and both MnO_2 followed a pattern of two steps single-electron reduction. Products of acetaminophen, analysed by UPLC-Tof-MS spectrometry, was found similar by both phases of MnO_2. This study supports that manganese dioxide involved a sequential single-electron reduction in the transformation of environmental pollutants, and is strongly limited by its electronic transfer ability other than active binding sites and adsorption sites. This study also provides a sight of oxidation of pollutants by δ-MnO_2 can be enhanced by interlayer cation exchanging.

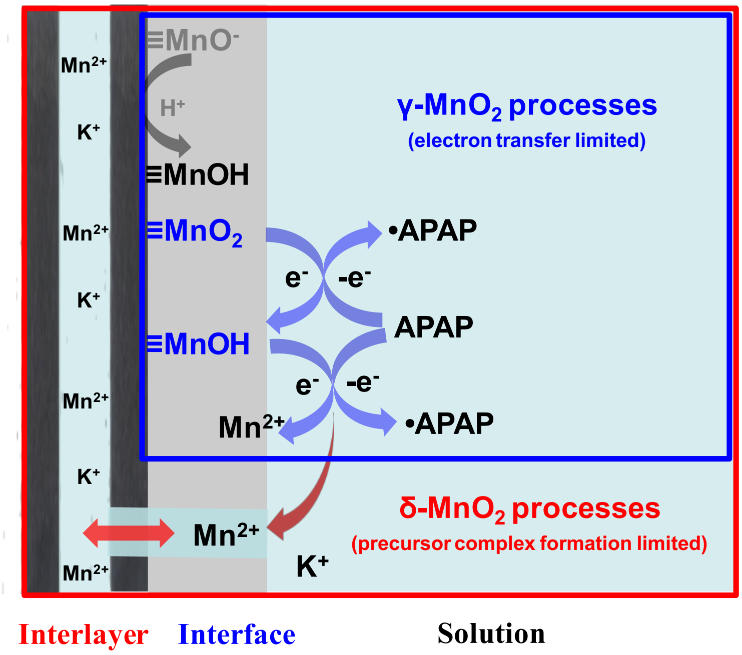

Figure 38: Process involved in the acetaminophen removal by different phases of MnO_2

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P32

Photo induced fatty acids polymerization and self-assembly into photoluminescent nanoparticles

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The sea surface microlayer (SML) is the top 1 millimeter of the ocean surface, where organic compounds such as fatty acids, amino acids, carbohydrates are highly enriched. Fatty acids widely present at air-water interface in the SML interface, are believed to be photochemical inert in the actinic region. However, due to highly surface-active, the air-water interface can promote some photochemical reactions which are difficult to occur. Herein, we report a formation process of fluorescent nanoparticles from fatty acid at the interface under photo irradiation. Light could induce fatty acids in situ producing dimers and self-assembly into vesicles (~100 nm). Simultaneously, unsaturated aldehydes, ketones and acids are formed upon light and encapsulated in vesicles. With particular confinement properties, the encapsulated small molecule compounds can be in situ transformed under light irradiation into fluorescent nanoparticles with a small diameter of 1.6 nm. Interestingly, since the extension of illumination time accelerates the photochemical reactions, the fluorescent color of the fluorescent nanoparticles can be controlled by adjusting the irradiation time. In addition, the as-obtained fluorescent materials have the advantages of low toxicity, good biocompatibility, excellent fluorescence and stability. They can be applied for fluorescence cells imaging.

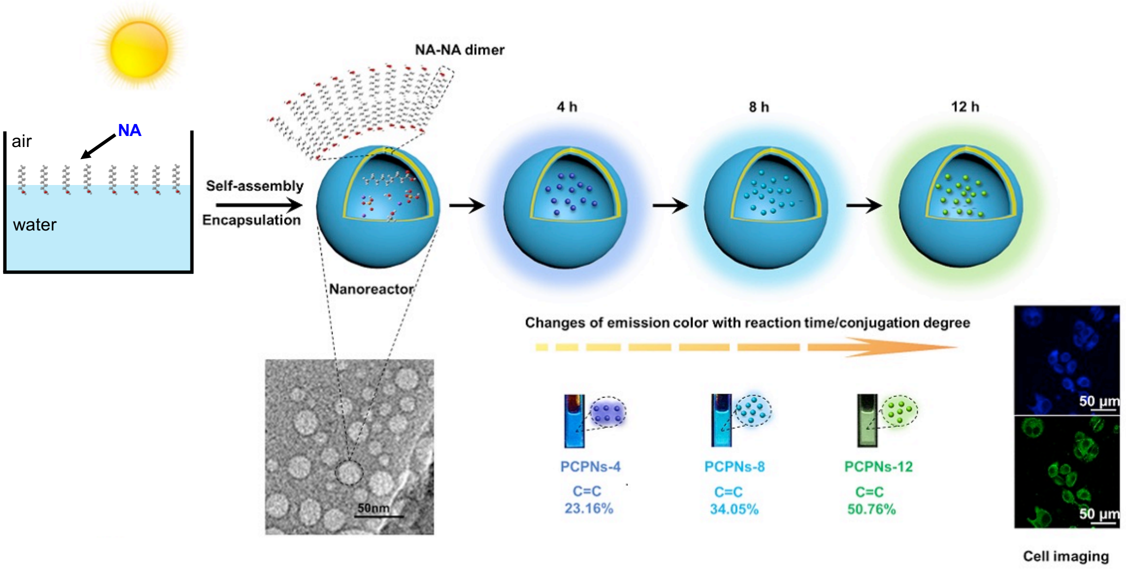

Figure 39: The in-situ formation of photoluminescent nanoparticles under photoirradiation.

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The application of NICA-Donnan model to the determination of Fe speciation in seawater

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The concentration of dissolved Fe (DFe) in the ocean is very low. Fe is essential for phytoplankton growth and it thus limits primary productivity in a major part of the global ocean (Boyd and Ellwood, 2010). The chemical reactivity and bioavailability of iron in seawater is a function of its' chemical speciation. However, the chemical speciation of Fe is still not fully understood (Boyd and Ellwood 2010, Gledhill and Buck 2012). DFe in the seawater tends to be strongly complexed by organic ligands, which increase the solubility of Fe in the seawater (Gledhill and Buck 2012). Adsorptive Cathodic Stripping Voltammetry (AdCSV) is the main method used to determine iron speciation in seawater. In this method Fe (III) in the samples is equilibrated with an artificial ligand (NN, 1-nitroso-2-naphthol) of known thermodynamic properties, which has the ability to absorb on the mercury, and be reduced by CSV. We used AdCSV to detect the concentration of $FeNN_3$ whilst varying the iron concentration at a fixed pH. We use non-ideal competitive adsorption in Donnan-like gels (NICA-Donnan model) with speciation program visual MINTEQ to interpret our titration data. A combination of generic NICA-Donnan parameters and those determined by Avendano et al. (2016), were applied within visual MINTEQ to calculate $FeNN_3$ concentrations for comparison with concentrations of $FeNN_3$ determined by AdCSV. In this study we used a "Multiwindow" titration approach, which utilized three different NN concentrations to further constrain the NICA-Donnan model. We measured Fe speciation in the central Celtic Sea water samples as a demonstration of the approach. The correlation between $[MeAL]_{model}$ and $[MeAL]_{experiment}$ suggests that the NICA-Donnan model, can be utilised to predict Fe speciation from ambient DOC and pH in seawater.

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Electrochemical oxidation prior to a biological treatment for Tetracycline removal

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This work aims to study the feasibility of degradation of tetracycline by a coupled process including electrochemical and biological ways.

Tetracycline antibiotic, widely used antibacterial in the world is of a special concern because of its extensive use in human and veterinary medicine, in aquaculture, as an additive to animal feeds, and it can also inhibit fungal growth in fruit trees. Between 30 and 90% of administrated tetracycline is excreted unchanged into the waste system. The presence of tetracycline residues and their potential to promote growth of resistant bacteria pose adverse health effects to humans.

Microbial toxicity biotests showed that at a relatively high concentration, tetracycline is not biodegradable and has inhibitory action. So, its direct degradation by conventional biological way is not appropriate. However, antibiotics could be fragmented by electrochemical treatment which seems to be an attractive way to destroy recalcitrant organic contaminants such as antibiotics.

Cyclic voltammetry with carbon and nickel electrodes revealed a good electrochemical activity for tetracycline. Such behavior led us to consider an electrochemical pre-treatment in order to decrease the toxicity and improve the biodegradability of studied antibiotic. Tetracycline can be oxidized in alkaline conditions on nickel at an oxidation potential of only 0.5 V/SCE, which is significantly lower than possible with a graphite-felt electrode (1 V/SCE) in neutral medium.

Electrochemical treatment was performed in a flow cell with a porous working electrode. The effect of the flow percolation rate was investigated. More than 95% of tetracycline was transformed. Electrolyzed solutions appeared biodegradable, since BOD_5/COD increased from 0 to 0.46 for untreated and pretreated TC at 0.7 V/SCE using modified nickel-modified graphite felt electrode, and from 0 to 0.39 at 1.6 V/SCE, using carbon felt electrode.

High performance liquid chromatography (HPLC), UV–visible spectroscopy and total organic carbon (TOC) analysis revealed that although a complete disappearance of tetracycline, the level of mineralization remained low insuring a significant amount of carbon for a possible subsequent biological treatment.

Mineralization yields did not exceed 44% and 31% with carbon felt and modified nickel-modified graphite felt electrodes respectively.

Adsorption of Emerging Micro-Pollutants in Clay Minerals

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Faith of micro-pollutants in soils has been the subject of directive proposals at the europena commission concerning soil quality. Indeed, contaminants stemming from industrialisation and the increasing use of chemicals in agriculture and daily life activities are responsible for their dissemination in the environment and in particular soils. These micro-pollutants are studied as they are discovered in the environment and because of their remanence; among them emerging micro-pollutants such as antibiotics, hormonal steroïds are of great concerns.

Clay minerals, are the main responsible species of the rentention of molecules in soil. Phyllosilicates, in particular smectites, are used to model clays because of their importante reactivity and their capacity to incorporate soil solution into their interlayer structure. Medicinal residues such as carbamazepine and paracetamol and pesticide such as glyphosate are considered as possible micro-pollutants.

Data obtained from analytical, christallographic and theoretical approaches are compared in order to measure and understand the ability of clay minerals to retain bio-organic molecules (emerging micro-pollutants).

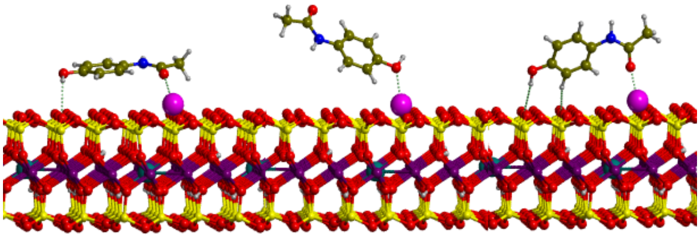

Figure 40: adsorption modes of paracetamol on the basal surface of Na$^+$-Montmorillonite

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Notes...

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Green processes for soil remediation and wastewater treatment

Multidisciplinary large-scale studies and field work

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Perspectives in energy conversion/storage and environmental remediation

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Prof. Dr. Irene Man Chi Lo
The Hong Kong University of Science & Technology, China

Prof. Dr. Jorge Gardea-Torresdey
The University of Texas at El Paso, USA

Dr. Thomas B. Hofstetter
Eawag institute, Switzerland

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