The 11th Interfaces Against Pollution

14-17 May 2021

Program and Abstract

Wuhan, China

Content

The 11th International Conference on Interfaces Against Pollution (IAP2021)

On behalf of the Organizing Committee, we are pleased to welcome you all to the **11th International Conference on Interfaces Against Pollution (IAP)**. 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 (The Netherlands, 2014), Lleida (Spain), and recently in La Grande Motte (France, 2018). Due to the global serious COVID-19 pandemic, IAP2021 conference will be conducted in a combination of on-site and on-line.

IAP conferences seek to provide a forum for researchers working in the interdisciplinary field of Environmental Science. The main focus of their work is on the importance of (bio) colloids and (bio) interfaces in natural reactive processes, both from fundamental and applied perspectives. The scope includes topics of social concern such as environmental protection, (bio) remediation of polluted sites, optimization of mineral resources, impacts of nanotechnology residues on the environment, and the key role played by interfaces in governing the fate and behaviors of pollutants in the environment. An adequate investigation of these issues necessarily requires joint experimental and theoretical expertise from physicists, physical chemists, biologists and geoscientists.

Following previous successful IAP conference series, IAP2021 provides a platform for academic researchers and industry participants working in the interdisciplinary field of environmental science and technology, with emphasis on the diverse roles played by colloids and interfaces in complex environmental processes and media, and in environmental sustainability.

The IAP2021 conference on-site will be located in Wuhan, an attractive city in central China. The Yangtze River and its greatest branch, the Hanshui River, flow across Wuhan and the city is surrounded by hundreds of lakes. We sincerely hope that in this strong city and in the pleasant May, we will provide a friendly atmosphere for researchers working together in the field of interfacial surfaces for a sustainable environment.

Chair: Wenfeng Tan	Huazhong Agricultural University, China
Co-chair: Liping Weng	Agro-environmental Protection Institute, Ministry of Agriculture and Rural Affairs, China
Co-chair: Peng Cai	Huazhong Agricultural University, China

Local Organization and International Committees

IAP2021 Local Organization

Conference organizers

- ✧ Huazhong Agricultural University (HZAU)

Co-organizers

- ✧ Agro-environmental protection institute, Ministry of Agriculture and Rural Affairs
- ✧ State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau
- ✧ State Environmental Protection Key Laboratory of Soil Health and Green Remediation

Contact Persons

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Website

- ✧ IAP2021: http://iap2021.hzau.edu.cn
- ✧ IAP main website: www.iapconferences.org

IAP International Advisory Committee

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Yandi Hu	Peking University
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Songhu Yuan	China University of Geosciences (Wuhan)

IAP2021 Program Overview

Beijing		**Paris**	**Washington***	**Theme**	
Friday **14 May**	9:00-22:00	3:00-16:00	21:00 (–1)-10:00	On-site registration (Educational Training Centre, Huazhong Agricultural University)	
Saturday **15 May**	8:20-8:40	2:20-2:40	20:20(–1)-20:40(–1)	Opening ceremony (On-site: Room A; On-line: Zoom platform 9035407588)	
Academic report				**On-site, Room A** **On-line, Zoom platform 9035407588**	**On-site, Room B** **On-line, Microsoft Teams**
Saturday **15 May**	8:40-9:20	2:40-3:20	20:40(–1)-21:20(–1)	Plenary Lecture (On-site: Room A; On-line: Zoom platform 9035407588)	
	9:20-12:00	3:20-6:00	21:20(–1)-24:00(–1)	Keynote & Oral Presentation	Keynote & Oral Presentation
	14:30-15:10	8:30-9:10	2:30-3:10	Plenary Lecture (On-site: Room A; On-line: Zoom platform 9035407588)	
	15:10-17:40	9:10-11:40	3:10-5:40	Keynote & Oral Presentation	Keynote & Oral Presentation
	19:00-22:00	13:00-16:00	7:00-10:10	Student Session	Student Session

Sunday **16 May**	8:30-9:10	2:30-3:10	20:30(–1)-21:10(–1)	Plenary Lecture (On-site: Room A; On-line: Zoom platform 9035407588)	
	9:10-11:40	3:10-5:40	21:10(–1)-23:40(–1)	Keynote & Oral Presentation	Keynote & Oral Presentation
	14:30-15:10	8:30-9:10	2:30-3:10	Plenary Lecture (On-site, Room A; On-line, Zoom platform 9035407588)	
	15:10-17:40	9:10-11:40	3:10-5:40	Keynote & Oral Presentation	Keynote & Oral Presentation
	19:00-21:00	13:00-15:00	7:00-9:00	Poster Presentations	Poster Presentations
Monday **17 May**	8:30-9:45	2:10-3:45	20:30(–1)-21:45(–1)	Keynote	Keynote
	9:45-10:45	3:45-4:45	21:45(–1)-22:45(–1)	Plenary Lecture (On-site: Room A; On-line: Zoom platform 9035407588)	
	10:45-11:00	4:45 -5:00	22:45(–1)-23:00(–1)	Award Ceremony (On-site: Room A; On-line: Zoom platform 9035407588)	
	11:00-11:20	5:00- 5:20	23:00(–1)-23:20(–1)	Closing Ceremony (On-site: Room A; On-line: Zoom platform 9035407588)	

IAP2021 Technical Schedule

(Beijing Time)

Friday 14 May

9:00-22:00	**On-site registration** **(**Educational Training Centre, Huazhong Agricultural University**)**

Saturday 15 May

8:20-8:40	**Opening ceremony** **Moderators: Wenfeng Tan** • Speech by President of HZAU, Prof. Zhaohu Li • Speech by President of IAP, Prof. Jérôme Duval
8:40-9:20	**Plenary Session (On-site, Room A; On-line, Zoom platform 9035407588)** **Moderators: Qiaoyun Huang**
	PL1: Biofilm/microbiome on anthropogenic surfaces: An emerging environmental issue Yong-GuanZhu, *Institute of Urban Environment and State, China*

9:20-10:10	**Keynote Session**	
	Room A/Zoom platform 9035407588 **Moderators: Qiaoyun Huang**	**Room B/Microsoft Teams** **Moderators: Peng Cai**
9:20-9:45	**KN1:** Kinetics of coupled redox processes at iron-water interfaces Paul G. Tratnyek, *OHSU-PSU School of Public Health, Oregon Health & Science University, USA*	**KN2:** Bioavailability of tetracycline to *escherichia coli* at solid-water interfaces Hui Li, *Michigan State University, USA*
9:45-10:10	**KN3:** Initial stage dynamics of flocculation of model colloids studied in the normalized mixing Adachi Yasuhisa, *University of Tsukuba, Japan*	**KN4:** PAHs in Soil-Plant System: Recent Advances Yanzheng Gao, *Nanjing Agricultural University, China*
10:10-10:40	***Tea break***	
10:40-12:00	**Oral Session**	
	Room A/Zoom platform 9035407588 **Moderators: Adachi Yasuhisa, Takumi Saito**	**Room B/Microsoft Teams** **Moderators: Yanzheng Gao, Tongxu Liu**
10:40-11:00	**Oral 1:** Hierarchical aggregation structures of humic acid by small-angle X-ray and neutron scattering Takumi Saito, *The University of Tokyo, Japan*	**Oral 2:** Electron transfer and elemental transformation processes between iron cycling bacteria and minerals Tongxu Liu, *Institute of Eco-environmental and Soil Sciences, China*

11:00-11:20	**Oral 3:** Hyphal-mineral interfacial processes drive fungal nutrient cycles Guanghui Yu, *Tianjin University, China*	**Oral 4:** Molecular mechanisms of lead binding to ferrihydrite-bacteria composites: ITC, XAFS and μ-XRF investigations Linchuan Fang, *Northwest A&F University, China*
11:20-11:40	**Oral 5:** Removal of PAHs in soil-plant system using domesticated indigenous microbial flora Jian Wang, *Nanjing Agricultural University, China*	**Oral 6:** Species of nickel(II) sorption or precipitation on minerals Xiaoli Tan, *North China Electric Power University, China*
11:40-12:00	**Oral 7:** Nonmonotonic effect of montmorillonites on the horizontal transfer of ARGs to bacteria Xiaojie Hu, *Nanjing Agricultural University, China*	**Oral 8:** Molecular-scale understanding of sulfate exchange from schwertmannite by chromate versus arsenate Xiaoming Wang, *Huazhong Agricultural University, China*
12:00-13:00	***Lunch***	
14:30-15:10	**Plenary Session (On-site, Room A; On-line, Zoom platform 9035407588) Moderators: Jérôme Duval**	
	PL2: Arsenic mobilization and removal – causes and solutions for the World's largest mass poisoning Andreas Kappler, *University of Tuebingen, Germany*	
15:10-16:00	**Keynote Session**	
	Room A/Zoom platform 9035407588 **Moderators: Jérôme Duval**	**Room B/Microsoft Teams** **Moderators: Jaume Puy**

15:10-15:35	**KN5:** Oceanic (Ba, Sr)SO_4 mysteries and aquatic Sr removal: Heterogeneous (Ba, Sr)SO_4 nucleation on organics Yandi Hu, *Peking University, China*	**KN6:** Coupled kinetics of arsenic adsorption/desorption and redox reactions at the mineral-water interfaces Zhenqing Shi, *South China University of Technology, China*
15:35-16:00	**KN7:** Environmental implications of humic acid and Fe oxides nanoparticle interaction Claudio Colombo, *University of Molise, Italy*	**KN8:** Redox reactivity of manganese oxides versus inorganic contaminants: Beneficial role of associated (in)organic ligands Bruno Lanson, *Université Grenoble Alpes, France*
16:00-16:20	***Tea break***	
16:20-17:40	**Oral Session**	
	Room A/Zoom platform 9035407588 **Moderators: Zhenqing Shi, Josep Galceran**	**Room B/Microsoft Teams** **Moderators: Bruno Lanson, Benedicte Prelot**
16:20-16:40	**Oral 9:** Iron oxide surfaces against chromate pollution Juan Antelo, *University of Santiago de Compostela, Spain*	**Oral 10:** The conditional affinity spectrum, a tool for the interpretation of adsorption data and adsorption isotherms Jaume Puy, *Universitat de Lleida, Spain*
16:40-17:00	**Oral 11:** The photocatalytic reduction of U(VI) over CdS/g-C_3N_4 Ping Li, Northwest Institute of Eco-Environment and Resources, CAS, China	**Oral 12:** Addressing the electrostatics of protons binding to humic matter beyond the Donnan level Jose Paulo Pinheiro, *Université de Lorraine, France*
17:00-17:20	**Oral 13:** AGNES and SSCP determination of free indium ion concentration	**Oral 14:** How to better explain ion specificity and competitive adsorption using calorimetric approaches

	Josep Galceran, *Universitat de Lleida, Spain*	Benedicte Prelot, *Université de Montpellier, France*
17:20-17:40	**Oral 15:** Proton binding to natural nano particles: specific and electrostatic interactions unravelled using charge density-pH curve Luuk K Koopal, *Wageningen University and Research, Netherland*	**Oral 16:** Critical role of collector surface roughness on the retention and release of nanoparticles in porous media Yan Liang, *Guangxi University, China*
18:00-19:00	***Dinner***	

Sunday 16 May

8:30-9:10	**Plenary Session (On-site, Room A; On-line, Zoom platform 9035407588)** **Moderators: Yandi Hu**	
	PL3: Nanoparticle interaction with biological membranes: the role of proteins Joel Pedersen, *University of Wisconsin-Madison, USA*	
9:10-10:00	**Keynote Session**	
	Room A/Zoom platform 9035407588 **Moderators: Qiaohui Fan**	**Room B/Microsoft Teams** **Moderators: Xionghan Feng**
9:10-9:35	**KN9:** Molecular geochemistry: systematic understanding of behaviors of various elements and new methods to support the approach Yoshio Takahashi, *University of Tokyo, Japan*	**KN10:** Biofilm biology-informed biofilm engineering for environmental biotechnology Bin Cao, *Nanyang Technological University, Singapore*
9:35-10:00	**KN11:** Humic acid-enhanced hydroxyl radical production during Fe(II)-bearing clay mineral oxygenation: changes of electron transfer pathway and number Songhu Yuan, *China University of Geosciences, China*	**KN12:** The spatiotemporal change of redox-sensitive elements in the soil-water interface and rice rhizosphere Zheng Chen, *Xi'an Jiaotong-Liverpool University, China*
10:00-10:20	***Tea break***	

10:20-11:40	**Oral Session**	
	Room A/Zoom platform 9035407588 **Moderators: Songhu Yuan, Juan Gao**	**Room B/Microsoft Teams** **Moderators: Zheng Chen, Anxu Sheng**
10:20-10:40	**Oral 17:** The formation and application of free radicals on clay surfaces Juan Gao, *Institute of Soil Science, China*	**Oral 18:** Aggregation of microplastic particles in the presence of humic acid: Effects of KCl and $CaCl_2$ solutions Azizul Hakim, *University of Chittagong, Bengal*
10:40-11:00	**Oral 19:** Simultaneous quantification effects of pH, calcium and phosphorus on the adsorption of arsenic in Paddy Soils Yingxuan Deng, *Henan Normal University, China*	**Oral 20:** Mechanistic understanding about Fe(II)-catalyzed ferrihydrite transformation Anxu Sheng, *Peking University, China*
11:00-11:20	**Oral 21:** Manganese oxide-coated zeolite decreases the Cd uptake of wheat plants in weakly alkaline soils Guohong Qiu, *Huazhong Agricultural University, China*	**Oral 22:** Electron transfer at the interface between Shewanella, pyrogenic carbon and nitroaromatic compounds Hefei Wang, Nanjing Agricultural University, China
11:20-11:40	**Oral 23:** Iron-montmorillonite-cyclodextrin composites as recyclable sorbent-catalysts for the adsorption and surface oxidation of per-fluorinated compounds Samapti Kundu, *Faculty of Civil and Environmental Engineering, Technion, Israel*	**Oral 24:** Highly enhanced As(III) oxidation at the surface of birnessite in the presence of pyrophosphate: depassivation effect & reaction mechanisms Xionghan Feng, *Huazhong Agricultural University, China*
12:00-13:00	***Lunch***	

14:30-15:10	**Plenary Session (On-site, Room A; On-line, Zoom platform 9035407588)** **Moderators: David Waite**	
	PL4: Machine learning exploration of biochar amendment in the immobilization of soil heavy metals Yong Sik Ok, *Korea University, Korea*	
15:10-16:00	**Keynote Session**	
	Room A/Zoom platform 9035407588 **Moderators: Yong Sik Ok**	**Room B/Microsoft Teams** **Moderators: Jerzy Zajac**
15:10-15:35	**KN13:** Nanoparticles and the mineral/biofilm/solution interface Marc F. Benedetti, *IPGP-Université de Paris, France*	**KN14:** Flow capacitive deionization (FCDI): does this interesting technology for water treatment and resource recovery have a future? David Waite, *University of New South Wales, Australia*
15:35-16:00	**KN15:** Cotransport of plastic particles with different types of colloids in porous media Meiping Tong, *Peking University, China*	**KN16:** Chemodynamic features of nanoparticles: insights into the dynamic life cycle of SARS-CoV-2 Raewyn Town, *Universiteit Antwerpen, Belgium*
16:0016:20	***Tea break***	
16:20-17:40	**Oral Session**	
	Room A/Zoom platform 9035407588 **Moderators: Raewyn Town, Laurent Duclaux**	**Room B/Microsoft Teams** **Moderators: Meiping Tong, Philippe Behra**
16:20-16:40	**Oral 25:** Macroscopic screening of competitive and co-operative effects in selective retention of pollutant ions	**Oral 26:** Study of glyphosate sorption onto chitosan molecularly imprinted polymers by surface plasmon resonance

	by charged solid surfaces Jerzy Zajac, *Institut Charles Gerhardt Montpellier, France*	Philippe Behra, *Université de Toulouse, France*
16:40-17:00	**Oral 27:** Adsorption of cationic dyes onto unmodified and modified biochar Yassine Bentahar, *Université Côted' Azur, Instite de Physique de Nice, France*	**Oral 28:** As(III) adsorption on Fe-Mn binary oxides: are Fe and Mn oxides synergistic or antagonistic for arsenic removal? Jingtao Hou, *Huazhong Agricultural University, China*
17:00-17:20	**Oral 29:** Activated carbon beads from chitosan for the NO_2 and formaldehyde removal from indoor air Laurent Duclaux, *Université Savoie Mont Blanc, France*	**Oral 30:** Hydration/Dehydration of adsorbed phthalic acid on goethite studied by IR spectroscopy and DFT+U Calculations Romain Botella, *Institut de Recherche de Chimie Paris, France*
17:20-17:40	**Oral 31:** Are the binding groups of Baltic coastal dissolved organic matter affected by seasonal variabilities? Pablo Lodeiro, *University of Lleida, Spain*	**Oral 32:** Evolution of Ni crystal chemistry and stability in birnessite during aging at room temperature and treatment at different temperatures Hui Yin, *Huazhong Agricultural University, China*
17:40-18:00	**Oral 33:** Natural organic matter-iron oxides interaction and effect on ion adsorption Liping Weng, *Agro-Environmental Protection Institute, Ministry of Agricultural and Rural Affairs, China &Wageningen University & Research, Netherland*	**Oral 34:** Effective heavy metal adsorption driven by electrochemically controlled redox of manganese oxides Lihu Liu, *Huazhong Agricultural University, China*
18:00-19:00	***Dinner***	

Monday 17 May

8:30-9:45	**Keynote Session**	
	Room A/Zoom platform 9035407588 **Moderators: Marcelo Avena, Xiao-Ying Yu**	**Room B/Microsoft Teams** **Moderators: Yoshio Takahashi, Mengqiang Zhu**
8:30-8:55	**KN17:** Multimodal imaging of oil-in-water bilgewater emulsion and biofilms Xiao-Ying Yu, *Earth and Biological Sciences Directorate, Pacific Northwest National Laboratory, USA*	**KN18:** Adsorption and oxidation of dissolved organic matter by iron and manganese oxides: insights from ESI-FT-ICR mass spectrometry Mengqiang Zhu, *University of Wyoming, USA*
8:55-9:20	**KN19:** Structural design and interface regulation of graphene based macro-materials for water purification Baoliang Chen, *Zhejiang University, China*	**KN20:** In-situ quick-scanning EXAFS measures rapid formation of surface precipitates at mineral-water interface Wei Li, *Nanjing University, China*
9:20-9:45	**KN21:** Electrochemical property of biochar and its application in environmental remediation Xinde Cao, *Shanghai Jiao Tong University, China*	**KN22:** Intercomparison and refinement of surface complexation models for U(VI) adsorption to goethite based on a metadata analysis Zimeng Wang, *Fudan University, China*
9:45-10:25	**Plenary Session (On-site, Room A; On-line, Zoom platform 9035407588)** **Moderators: Marcelo Avena**	
	PL5: Stability of U(VI) on surfaces of montmorillonite and UO$_2$ Daniel E. Giammar, *Washington University in St. Louis, USA*	

10:25-10:45	***Tea break***
10:45-11:00	**Award Ceremony** (On-site, Room A; On-line, Zoom platform 9035407588) **Moderators: Liping Weng** • Best Poster • Best student presentation
11:00-11:20	**Closing Ceremony** (On-site, Room A; On-line, Zoom platform 9035407588) **Moderators: Michael Sander** • Speech of welcoming to IAP2022
12:00-13:00	***Lunch***

Student Session

(Saturday, 15 May; 19:00-21:30Beijing Time)

19:00-21:30	**Room A/Zoom platform 9035407588** **Moderators: Xiaoli Tan, Xiaoming Wang**	**Room B/Microsoft Teams** **Moderators: Linchuan Fang, Jingtao Hou**
19:00-19:15	**SS1:** Enhanced catalytic activity of OMS-2 for carcinogenic benzene elimination by tuning Sr^{2+} contents in the tunnels Chunlan Ni, *Huazhong Agricultural University, China*	**SS2:** Transport of enzymes in quartz sand column partially coated with goethite: effects of pH and humic acid Yan Li, *Huazhong Agricultural University, China*
19:15-19:30	**SS3:** Nano-gold decorated TiO_2, and ZnO for NO_x degradation: new photocatalytic materials for the improvement of air quality Castelló Lux Kevin, *Laboratoire de Chimie de Coordination de Toulouse, France*	**SS4:** Reactive transport of REE: surface complexation with quartz surfaces and modeling investigations Muhammad Muqeet Iqbal, *Universite de Rennes, France*
19:30-19:45	**SS5:** Fe-Chitosan Complexes for oxidative degradation of emerging contaminants in water: structure, activity, and reaction Mechanism Giulio Farinelli, *Politecnico di Torino, Italy*	**SS6:** Evaluation of heavy metal availability in soils near former zinc smelters by chemical extractions and geochemical modelling Hui Gao, *Wageningen University & Research, Netherland*
19:45-20:00	**SS7:** A novel phosphate-modified calcite adsorbent using for fluoride removal: Synthesis, efficiency, and defluoridation mechanism	**SS8:** Prediction of nano-magnetite stoichiometry in aqueous solution Phoomipat Jungcharoen, *University of Rennes, France*

	Jingzhao Wang, *Nanjing University, China*	
20:00-20:15	**SS9:** Coupled effects of Mn(II), pH and anionic ligands on the reactivity of nanostructured birnessite Qinzhi Li, *École Nationale Supérieure de Chimie de Rennes, France*	**SS10:** The influence of the gel or resin layer thicknesses on the measurement of metal accumulation in DGT Jordi Sans-Duno, *Universitat de Lleida, Spain*
20:15-20:30	**SS11:** Heterogeneous degradation of refractory pollutants by peroxymonosulfate activated by cobalt-doped FeS Yanting Pan, *Huazhong Agricultural University, China*	**SS12:** Evaluation of dyes sorption onto hierarchical Faujasite based on multiscale approaches Marwa Assaf, *Université de Montpellier, France*
20:30-20:45	**SS13:** Adsorption capacity of the corrosion products of nanoscale zerovalent iron for emerging contaminants Junmin Deng, *Ecolenationalesupérieure de chimie de Rennes, France*	**SS14:** Selective sorption of phytate and orthophosphate on ferrihydrite with different aggregation Zhen Hu, *Huazhong Agricultural University, China*
20:45-21:00	**SS15:** Microstructure of Al-substituted goethite and its adsorption performance for Pb(II) and As(V) Yu Liang, *Huazhong Agricultural University, China*	**SS16:** Inter-laboratory validation of vapor pressure measurements of two endocrine-disrupting molecules: 4-tert-octylphenol & 4-n-octylphenol using gas saturation and static method Joanna Farhat, *Université Claude Bernard Lyon, France*
21:00-21:15	**SS17:** Photosensitized degradation of paracetamol by rose bengal-modified clays and alginate materials/rose-bengal Yanet Mayer, *Universidad Nacional del Sur, Argentina*	**SS18:** Water dispersible colloids and related nutrient availability in Amazonian Terra Preta soils Qian Zhang, *Institute of Bio- and Geosciences, Agrosphere (IBG-3), Forscungszentrum Jülich GmbH, Germany*

21:15-21:30	**SS19:** Molecular understanding of humic acid-promoted hydrolysis of phytate through stabilizing a conserved catalytic domain in phytase Xinfei Ge, *Huazhong Agricultural University, China*	**SS20:** A new protocol for executing acid/base titration on organic matter applied to seven new IHSS batches Marawit Tesfa, *Université Rennes, France*
21:30-21:45	**SS21：**Nanoscale Imaging of Simultaneous Occlusion of Nanoplastics and Glyphosate within Soil Minerals Jialin Chi, *Huazhong Agricultural University, China*	**SS22:** As(III) adsorption-oxidation behavior and mechanisms on Cr(VI)-incorporated schwertmannite Hong Ying, *Huazhong Agricultural University, China*
21:45-22:00	**SS23:** Molecular sorption mechanisms of Cr(III) to organo-ferrihydrite coprecipitates using synchrotron-based EXAFS and STXM techniques Xing Xia, *Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, China*	**SS24:** Molecular mechanisms of cadmium sorption to rape straw biochars using ^{13}C nuclear magnetic resonance spectroscopy and Cd L_3-edge X-ray absorption near-edge structure Yihao Wang, *Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, China*

Poster Presentations

(Sunday, 16 May; 19:00-21:00 Beijing Time)

P1: Building an effective concentration signature for Zn availability from 4 techniques to a stream
Kevin Rosales-Segovia, *Universitat de Lleida, Spain*

P2: Physical and chemical fractionation of soil organic carbon in relation to long-term phosphate fertilization
Yilina Bai, *Wageningen University, Netherlands*

P3: Photocatalytic activation of sulfite by maghemite (γ-Fe_2O_3) towards iohexol degradation with magnetic separation
Cheng Wang, *Huazhong Agricultural University, China*

P4: Passivation of heavy metals in landfill soils of mountain villages by phosphorus-containing substances
Li Huang, *Huazhong Agricultural University, China*

P5: Effects of organic matter–goethite interactions on reactive transport of nalidixic acid: Column study and modeling
Wei Cheng, *South Central University of Nationalities, China*

P6: Coagulation and sedimentation of imogolite: effect of pH and salt concentration
Yuji Yamashita, *University of Tsukuba, Japan*

P7: Influence of titanium dioxide nanoparticles on metallic trace elements behaviour in soils
Quynh Nguyen-Phuong, *University of Reims Champagne-Ardenne, France*

P8: Ultrasound-synthesized zero valent iron nanoparticles for Cr(VI) removal, application for the treatment of metal surface processing wastewater
N. Bounab, *Université Savoie Mont Blanc, France*

P9: Wood wastes: from an environmental burden to efficient biochars for pharmaceutical molecules removal in aqueous solution

Laurent Duclaux, *Université Savoie Mont Blanc, France*

P10: Development of new materials for the adsorption of arsenic (V)

Carina Luengo, *INQUISUR, Universidad Nacional del Sur, Argentina*

P11: Synthesis of montmorillonite-alginate beads applied to the kinetic study of paraquat adsorption

Mariana Etcheverry, *Universidad Nacionaldel Sur (UNS), INQUISUR-CONICET, Argentina*

P12: Removal of caffeine from water sources using alginate/carbon nanotubes beads

Orduz Angie, *Universidad Nacional del Sur, Argentina*

P13: Use of mosses for heavy metals removal from the environment

Sarah Fiol, *Universidad de Santiago de Compostela, Spain*

P14: Mesoporous silica: Is it really effective for decontamination of water bodies?

Julián Ortiz Otalvaro, Maximilano Brigante, *Universidad Nacionaldel Sur - INQUISUR, Argentina*

P15: The role of mineral structure in metal speciation and cycling in contamined soil

Wei Zhao, *Northwest A&F University, China*

P16: Phosphate speciation on Al-substituted goethite: ATR-FTIR /2D-COS and CD-MUSIC modeling

Jinling Xu, *Shandong Normal University, China*

P17: Selective and quantitative adsorption mechanisms of soil humic substance on multi-component minerals

Hongfeng Chen, *Three Gorges University, China*

P18: Fraction distribution of heavy metals and its relationship with iron in polluted farmland soils around distinct mining areas

Wantong Zhao, *Huazhong Agricultural University, China*

P19: Facet-dependent surface charge and Pb^{2+} adsorption characteristics of hematite nanoparticles: CD-MUSIC-eSGC modelling

Mingxia Wang, *Huazhong Agricultural University, China*

P20: Impact of low-molecular-weight organic acids on selenite immobilization by goethite: Understanding a competitive-synergistic coupling effect and speciation transformation

Dun Fang, *Hubei Minzu University, China*

P21: Modifying MIL-100(Fe) through co-growing iron oxides to enhance its adsorption for selenite

Shiyong Wei, *Hubei Minzu University, China*

Biofilm/microbiome on anthropogenic surfaces: An emerging environmental issue

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Human civilization has created numerous synthetic or modified natural surfaces, such as glass, metal and plastics. Collectively, I would like to term these “non-natural” surfaces as anthropogenic surfaces, and among them, plastics represent one of most distinctive ones, both in terms of abundance and properties. Like other surfaces, microorganisms can colonize anthropogenic surfaces to form an adherent and cohesive mat-so called biofilm. Microbial communities in biofilms often exhibit distinct physiology and functions as compared with planktonic cells.
Although humans are discharging numerous debris into the environment, plastic debris is by far the most abundant one. Moreover, as a hydrophobic substrate, plastics can readily accumulate organic and inorganic pollutants in the environment, which can be considered as a novel ecological niche for microorganisms. In this talk, we will discuss the development of biofilms on different plastic surfaces, both in water and soil environment. We will specificly examine the recruitment of microorganisms by different plastic surfaces and delineating the driving forces that shape microbial communities on plastic surface. We will further investigate the presence of human pathogens and antibiotic resistance genes in the plastisphere. Finally, we will discuss the needs of future research on microbiomes in anthropogenic surfaces.

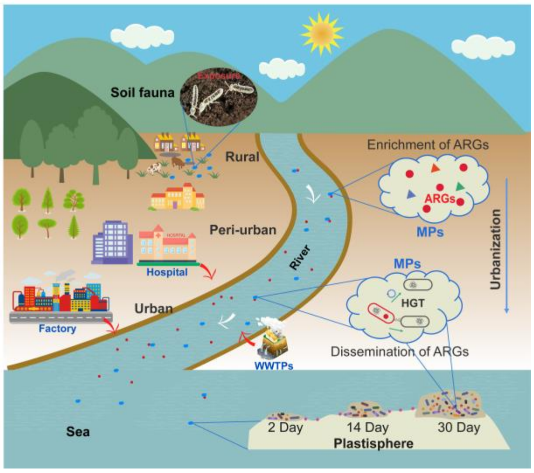

Figure 1: Schematic illustration of the antibiotic resistome and microbiome carried by plastic debris.

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KN1

Kinetics of coupled redox processes at iron-water interfaces

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The interface between granular zerovalent iron (ZVI) and aqueous media is a complex and dynamic system that has been the subject of a vast amount of research; primarily because it controls corrosion of ferruginous metals, but recently because it has become widely used to remove a variety of contaminants from water. Some of this research has used microscopy, spectroscopy, and/or electrochemical methods for *direct* characterization of the structure and reactions at the interface. However, the majority of studies—especially those motivated by environmental remediation applications—rely mainly on *indirect* characterization based on interpretation of changes in solution phase chemistry.

It is very common for new studies of contaminant removal in aqueous slurries of granular ZVI to report large amounts of solution phase chemical data (concentration of contaminants and products, dissolved Fe(II), DO, Eh, pH, etc.) measured synchronously over time in batch experiments performed under a range of initial conditions (iron type and pretreatment, buffer and pH, etc.). These data usually show complex patterns that are difficult to intepretate simply by inspection of, and comprison among, conventional concentration vs. time plots. This problem is not unique to research involving ZVI, but it is especially acute because of the very large volume of new studies on ZVI that take this experimental approach.

In an effort to overcome this challenge, we have found it can be useful to rearrange the data into a format that we call “time series correlation” (TSC) plots. In a TSC plot, pairs of measured parameters are plotted on x and y and the time series is represented as f(z). Data obtained under different conditions can be superimposed, resulting in a unique perspective on the coupled reactions between ZVI and species in solution. This presentation will use the history of our use of TSC plots to link a variety of advances we have made in understanding reactions involving ZVI in batch, model system studies with a variety of organic and metal(loid) oxyanion contaminants. Fundamental issues that will be addressed include the relative significance of electron and atom transfer reactions in dechlorination, the efficiency of contaminant reduction vs. reduction of water to hydrogen, and the effects of competing parallel contaminant reduction reactions.

Bioavailability of tetracycline to *escherichia coli* at solid-water interfaces

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Tetracyclines are a class of antimicrobials frequently found in the environment originating primarily from their extensive use in human medicine and in animal production. Tetracycline is bioavailable to bacteria and evoke the expression of antibiotic resistance genes in aqueous solution. The extent of bioavailability is dependent on its speciation in solution. An unanswered research question is whether tetracycline sorbed to soils is still bioavailable and pose selective pressure on bacteria for development and proliferation of antibiotic resistance. We used a bioreporter *E. coli* MC4100/pTGM strain to probe the bioavailability of tetracycline sorbed by soils and soil components. The results indicated that the direct contact of *E. coli* cells to soil surfaces represents an important pathway for bacteria to access soil-sorbed tetracycline and activate the corresponding antibiotic resistance genes. In soil suspensions, reducing solution volume rendered more tetracycline to become bioavailable the bacteria attached to sorbent surfaces. The strong fluorescence emission from bioreporter on sorbent surfaces indicated that sorbed tetracycline is still accessible by bacteria. The results of agar diffusion assay, microscopic visualization and model simulations revealed the bioavailability of tetracycline sorbed by soils under unsaturated conditions. The bioavailability of soil-sorbed tetracycline was much higher for a sandy soil than other soils because of the faster diffusion of tetracycline in coarse-textured soils. Decreasing bioavailability of soil-sorbed tetracycline was observed at lower soil water potential, resulting likely from the reduction of tetracycline diffusion in soil pore water at smaller matric potential, and/or suppression of tetracycline uptake by *E. coli* at lower osmotic potential. Tetracyclines sequestrated in biochar pores demonstrated the reduced bioavailability. In summary, soil-sorbed tetracycline could still exert selective pressure on the bacteria at soil surfaces. Bacterial attachment to soil surfaces is very common in soils, and this attachment could lead to the selective pressure from soil-sorbed antibiotics to bacteria for potential preservation of antibiotic resistance. The sequestration of tetracycline in biochar micropores could effectively mitigate the bioavailability of antibiotics to surface attached bacteria.

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KN3

Initial Stage Dynamics of Flocculation of Model Colloids Studied in the Normalized Mixing

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We have developed the experimental procedure of colloid mixing with which collision process between colloidal particles and between the reference colloidal particle and adsorbing polymers can be evaluated. Although the first question on the additivity of peri-kinetic and ortho-kinetics is remained, Kolmogoroff hypothesis on the isotropic turbulence has been verified to be valid on the estimation of flocculation rate. The developed procedure has been applied to various types of flocculation. The revealed dynamics are:

1) The role of polymer conformation in solution.

2) The swelling behavior of polyelectrolyte under the condition of low ionic strengh.

3) Additional attractive force due to electorstatic interaction.

4) Folding procee of nuetral polyer and polyelectrolyte on the surface of collidal particles.

5) Effect of charge density of polyelectrolyte chains.

6) Formation of aggregate of macromolecules during incubation.

7) Effec of PIC formation

8) Effect of microgel formation and their aggregate formation

9) Inhibitory effects of flocculation by the co-presense of likely-charged polymer to that of the particle.

10) Effect of molecular branching structure.

Further information based on the electrokinetics and estimation of hydrodynamic layer thickness has revealed picture on the dynamic behavior of polymar flocculant on the surface of colloidal particles.

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PAHs in soil-plant system: Recent advances

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Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants due to their mutagenicity, potential toxicity, and carcinogenicity. Their occurrence in soil-plant system poses a potential public health hazard and cause high incremental lifetime cancer risks. This work describes the recent advances of soil PAHs concerning with their sources, phytoavailability, plant uptake, ecotoxicology, and endophyte-related cleanup techniques. PAHs have been found with high concentrations in some commercial and laboratory-produced biochars, and the application of these biochars to soils may result in plant PAH contamination and human cancer risk. Bound residues will be formed when PAHs entering into soil. However, the root exudates could release these bound fractions in rhizosphere, and this work affirmed the phytoavailability of bound PAH residues in field contaminated soils aged for years. The released PAHs in soil will be absorbed by plants, and the distribution and metabolisms of PAHs in subcellular fractions were clarified. PAHs mainly distributed in cell solid fractions. How to reduce the PAHs in plant is of great concerns. This work found that isolation of PAH-degrading endophytic bacteria and colonization back to plants could dramatically reduce the plant PAH concentrations and human risks. We think that more attentions in future could be addressed on PAH derivatives and their molecular ecotoxicology in the soil environments.

Oral 1

Hierarchical aggregation structures of humic acid by small-angle X-ray and neutron scattering

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Humic substances (HSs) are an important class of natural organic matters, originating from degradation and condensation of animal, plant, and microbial residues. HSs are not molecular entities with distinct structures, but can be considered as collections of organic molecules with certain physicochemical properties in common. HSs play important roles for the fate of pollutants and nutrients in soil and aquatic envronments. In particular the aggregation and disaggregation of HSs are vital processes that affect the aforementioned roles of HSs, modulating available functional groups for metal ions, apparent hydrophobicity for organic molecules, and electrostatic potential. Although macroscopic aggregation of HSs has been studied by various researchers, their aggregation structures in nano- and meso-length scales are poorly understood. Thus, the objective of this study is to elaborate the aggregation structures of HSs by combining small-angle scattering of X-ray and neutron. The use of the different probes for scattering enabled us to get insights on heterogeneous aggregation of HSs.

HS samples examined in this study are HA commercially available from Sigma-Aldrich (PAHA) [1] and that extracted from deep sedimentary groundwater (HHA) [2]. The sampels for small-angle X-ray scattering (SAXS) and neutron scattering (SANS) ware prepared at 2 g/L in D_2O (>99.8%) as a function of pD in the presence of 5 mM NaCl. The time-of-flight SANS measurements were performed at the BL-15, TAIKAN of the Materials and Life Science Experimental Facility (MLF) in the J-PARC (Tokai, Japan), a spollation neutron source. The SAXS measurements were carried out at the BL-6A of the photon factory, KEK (Tsukuba, Japan) with monochromized X-ray at λ = 1.5 Å. Macroscopic coagulation of the HAs were also examined as a function of pH in the presence of 5 mM NaCl by measuring the TOC concentrations of the supernatants after centrifugation.

No significant decrease of the dissolved concentration was observed for PAHA over the entire pH range (pH 4-9). On the other hand, the concentration of dissolved HHA was decreased with a decrease of pH at pH < 6 due to coagulation. SAXS and SANS exhibited increases of the scattering intensities with a decrase of the scattering vector, *q*, for both PAHA and HHA regardless of the solution condition. This was indicative of the formation of aggregates even for PAHA, for which no coagulation was observed, and HHA at relatively high pH(D). The comparision of SAXS and SANS profiles exhibietd considerable differences of the scattering profiles for PAHA. As X-ray and neutron probe different moieties of a scatter, this suggested the heterogeneity of the PAHA aggregates. Meanwhile, the SAXS and SANS profiles largely overlaped for HHA, indicating the formation of homogeneous aggregates. Furhter inspection of the SAXS and SANS profiles of PAHA revealed a picture of its aggregation structure as electron-rich cores embedded in hyrogen-rich shells. This view will be tested by a theoretical modeling in the talk of the conference.

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Oral 2

Electron transfer and elemental transformation processes between iron cycling bacteria and minerals

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The main solid phases in soils and sediments include minerals, organic matters, and microbes, and their interactions play vital roles in elemental cycles and contamiant degradation[1]. The electron transfer among iron cycling bacteria, organics, and minerals has been paid great attention. In this study, the electron transfer and the elemental transformation processes among mineral-mediator-microbe were investigated, and the main findings include: 1. By employing the in situ spectral methdod, the releasing mechanism of extracellular c-Cyts produced by MR-1 was disclosed and it likely played a role in extracellular electron transfer under electron acceptor-limited conditions (Figure 1a)[2]; the new phenomena of electron mediator stimulating the biofilm formation was found and the underlying mechanism was revealed (Figure 1b) [3]. 2. The new evidence of electron transfer from Fe(II) to OMEs was obtained[4]; the shift in conduction band energy level was found as the key electrochemical evidence, due to the electron/charge accumulation on the hematite surface, and the new pathway of conduction band-mediated electron transfer was proposed (Figure 1c). 3. The dual N-O isotopic fractionation mechanism during microbially mediated coupling process of nitrate reduction and Fe(II) oxidation was demonstrated[5]; the relative significance of the biotic and abiotic processes was quantitatively assessed[6]. The findings could promote the interdisciplinary integration of soil chemistry, and soil microbiology, and have provided a theoretical basis for soil pollution control. In the future work, the new mechanisms of soil electron transfer and the coupling microbial-chemical-physical processes and environmental implications will be comprehensively investigated.

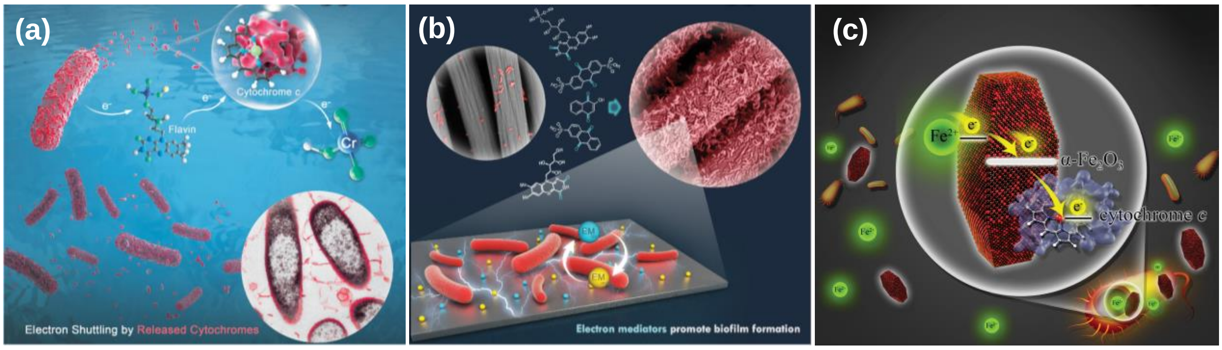

Figure 1: Electron transfer mechanisms between iron cycling bacteria and minerals

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Oral 3

Hyphal-mineral interfacial processes drive fungal nutrient cycles

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The ability of fungi to weather a wide range of minerals influences plant nutrition and enhances global biogeochemical cycles of life-essential elements. The fungus-mineral interface plays a key role in weathering, but the specific mechanisms underlying these processes remain poorly understood. Here, we examined fungal-mineral weathering using hematite and Trichoderma guizhouense. We showed that of the hematite associated with hyphae, approximately 15% was converted to the secondary mineral ferrihydrite. These biogenic ferrihydrite nanoparticles are extensively formed at the interface between an actively growing fungus and an iron-containing mineral, hematite. Importantly, superoxide radicals were detected at the hyphal tips and along the whole hyphae. During cultivation, a high concentration (~1000 nM) of hydroxyl radical was also detected. Synchrotron radiation based spectromicroscopies at fungus-mineral interfaces suggest that fungus hyphae alter the local redox state of iron and thus are redox-active. These findings indicate that fungus-initiated catalytic reactions occur at hyphalmineral interfaces, in view of the fact that superoxide does not diffuse far from the site of formation. These biogenic nanoparticles formed through the fungus-hematite interactions can behave as mimetic catalysts, similar to nanozymes that imitate peroxidase, which scavenges hydrogen peroxide for the mitigation of potential cytotoxicity (Figure 1). Evidence from various X-ray spectroscopic analyses indicated that non-lattice oxygen in the nanomaterials was chiefly responsible for this catalytic activity, rather than through the conventional mechanisms of iron redox chemistry. Cryo-scanning electron microscopy, high-resolution (~30 nm) 3D volume rendering, and biomass analyses further confirmed that the organism was active and capable of mediating the catalytic reactions. We therefore hypothesize that this confers an advantage to the organism in terms of protection from oxidative stress and ensuring the acquisition of essential iron (Figure 1). These findings constitute a significant step forward in understanding the ways that fungi make minerals available to biological systems and raise new questions about the roles of biogenic nanomaterials in the coevolution of the lithosphere and biosphere.

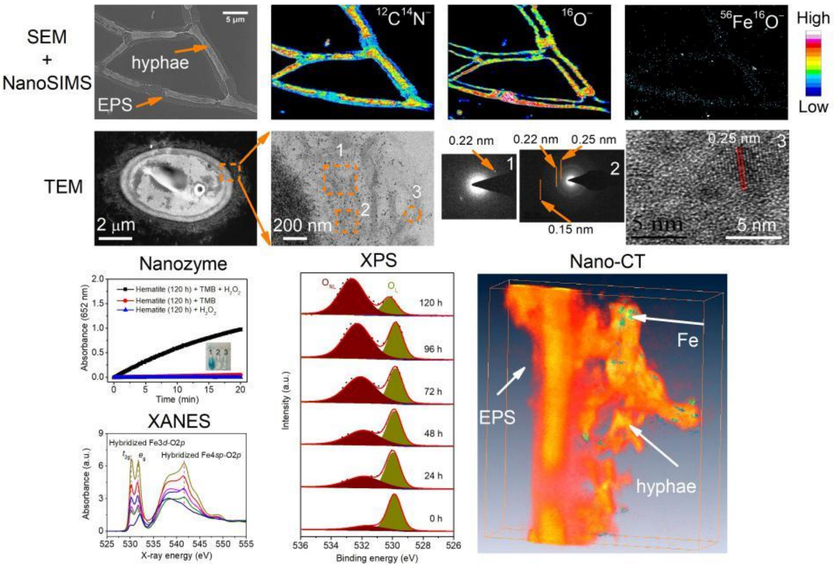

Figure 1: Fungal mineral coatings and their nanozyme activities

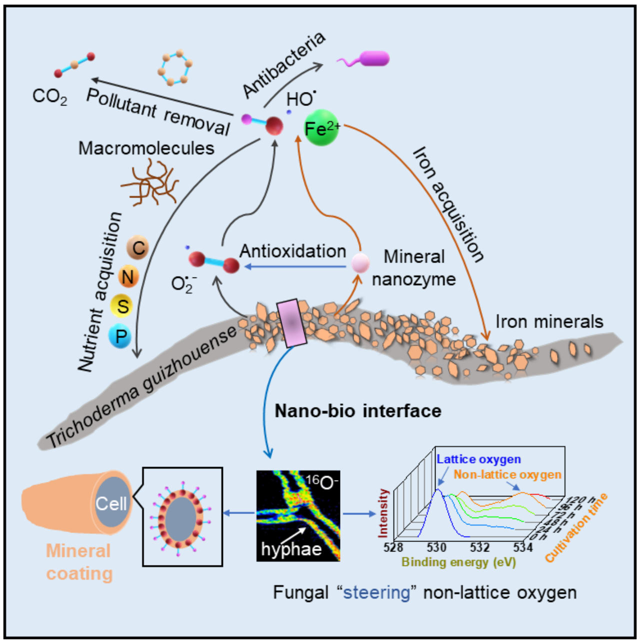

Figure 2: Proposed mechanisms of fungal nanophase particles driving nutrient acquisition

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Oral 4

Molecular Mechanisms of Lead Binding to Ferrihydrite-Bacteria Composites: ITC, XAFS and *μ*-XRF Investigations

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Binding of Pb(II) to ferrihydrite–*Bacillus subtilis* composites formed in the presence of bacterial cells were investigated through macroscopic and microscopic techniques. Diffuse layer model (DLM) fitting and isothermal titration calorimetry (ITC) analysis indicated that the hydroxyl group played a key role in Pb(II) sorption onto composites by masking reactive sites, such as carboxyl and phosphoryl groups of bacterial cells. Negative enthalpy (from -39.29 to -57.87 kJ mol^{-1}) and positive entropy (from 135.61 to 193.47 kJ mol^{-1}) of Pb(II) sorption onto composites revealed that inner-sphere complexes formed through exothermic reactions and was driven by both entropy and enthalpy. Spatial distribution of these inner-sphere species at varied Pb(II) loading demonstrated that interactions between Pb(II) and bacterial cells preceded that of mineral components in composites, using microfocus X-ray fluorescence spectroscopy (*μ*-XRF) maps and microfocus X-ray absorption near edge structure (*μ*-XANES) spectra. Combined with bulk Pb L_{III}-edge X-ray absorption fine structure (XAFS) spectrum, we inferred that mononuclear bidentate edge-sharing hydroxyl-Pb complexes, monodentate mononuclear carboxyl-Pb and phosphoryl-Pb complexes predominantly contributed to Pb(II) inner-sphere binding with mineral and bacterial fractions in composites, respectively (Fig.1). The molecular binding mechanisms obtained in this study provide further insight into the sequestration and migration of toxic metals in natural environments.

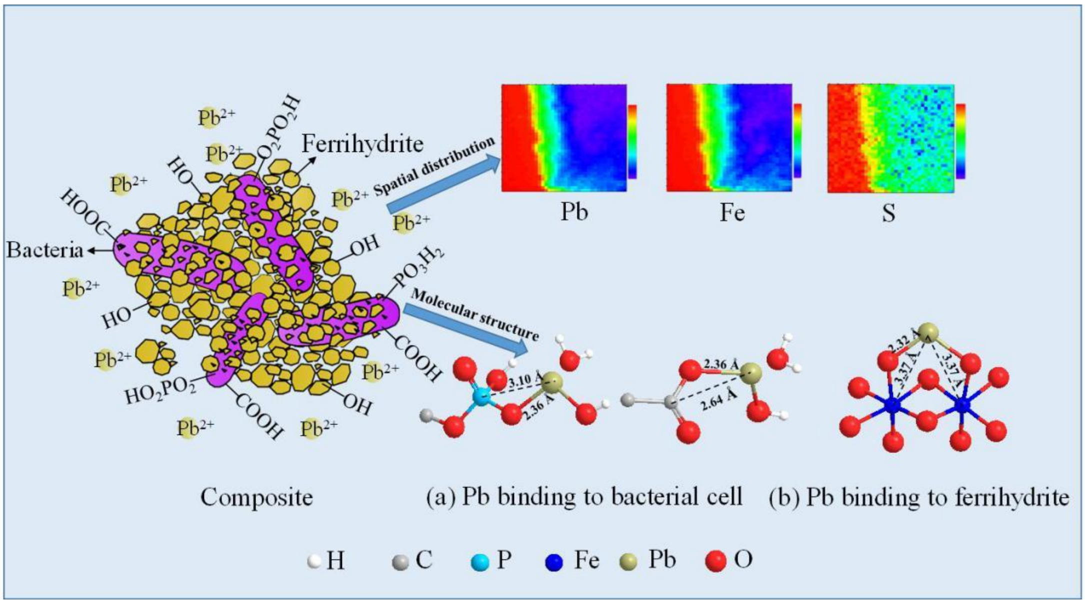

Fig.1 Predominant molecular structure of Pb(II) binding with ferrihydrite-B. subtilis composites

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Removal of PAHs in soil-plant system using domesticated indigenous microbial flora

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Polycyclic aromatic hydrocarbons (PAHs) in soils pose a risk to ecological and human health. The use of PAH-degrading bacteria to reduce PAH concentrations in soil-plant system has received much attention for their economical, efficient, and environmentally friendly characteristics. However, exogenous microorganisms do not have the competitive advantage and the broad spectrum of degradation under in situ conditions, which often fail to achieve the expected restoration goals. Particular indigenous microbial flora is dominant in PAH-contaminated soil and plant because of natural selection resulting from the pressure of PAH contaminants, and the utilization of a domesticated indigenous microbial flora as an inoculum may be advantageous to efficiently degrade PAHs in the soil-plant system. To this end, this paper aimed to obtain a domesticated indigenous microbial flora with a high efficiency in degrading 16 US EPA-PAHs, and their performance in the PAHs degradation after introduced into the soil-plant system were well studied. Our results show that the introduction of this bacterial community to the soil-plant system reduced the PAHs concentration in soil-plant system, and the 16 EPA priority PAHs decreased from 95.23 to 23.41 mg/kg over 35 days in the soil, particularly HMW PAHs. The PAHs concentration in plants and the incremental lifetime cancer risk (ILCR) values were also decreased. The application of bacterial community increased the copy numbers and relative abundances of PAHs degradation gene such as nidA and bphA1 in soil and plant, and therefore decreased soil PAH contents in the soil-plant system. These results indicate that adding the native bacterial community to contaminated soil may be a feasible and environmentally friendly method to clean up PAHs in agricultural soil.

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Species of nickel(II) sorption or precipitation on minerals

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Availability of Ni(II) for bio-uptake and transport in the environment is controlled by the sorption and/or precipitation process and speciation of Ni(II) on mineral surfaces. Nickel ion can interact with the oxide surface via its –OH group, while the ion exchange also contributes to the sorption of Ni(II) on montmorillonite and other minerals.

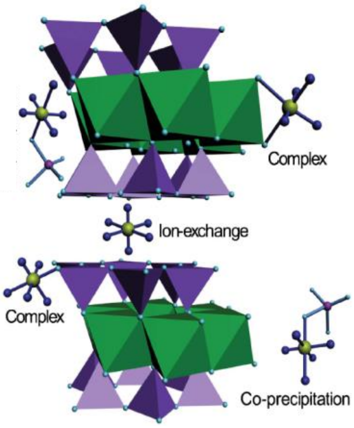

Figure 1 Sorption sites for Ni(II) on montmorillonite.

The formation of mixed metal precipitates has been a significant mechanism for the immobilization and elimination of heavy metal ions. The growth of Ni-Al layered double hydroxide (LDH) phase is verified on the surface of γ-Al_2O_3 and aluminosilicate surface. The coexisting silicate can influence the release of Al^{3+} and then the component of precipitates, lead to the less stable Ni-Al LDH. The results have great implications regarding the factors affecting the transfer and retention of metal ions in natural systems and therefore require attention in the natural environment.

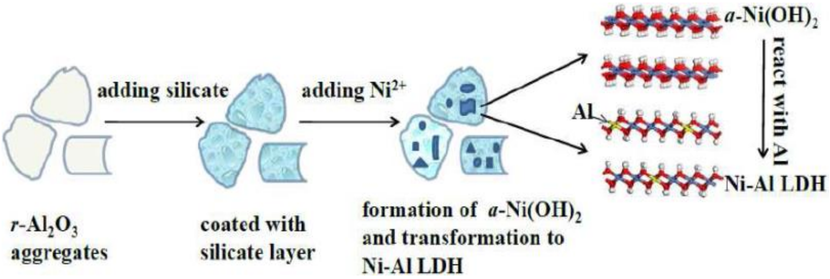

Figure 2 Effect of silicate on the precipitation of Ni(II) on γ-Al_2O_3.

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Oral 7

Nonmonotonic Effect of Montmorillonites on the Horizontal Transfer of Antibiotic Resistance Genes to Bacteria

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Bacterial transformation is important to the transmission of antibiotic resistance genes (ARGs) in soils, and soil pore water is recognized as a hot spot for dissemination of ARGs. However, little is known about how concentrations and sizes of clay particles in soil pore water influence the horizontal transfer of ARGs. This study investigated the horizontal transfer of an antibiotic resistant plasmid (pUC19) into competent *Escherichia coli* cells with or without montmorillonites (MMTs, 0−2 g/L) with average sizes of 1568 nm (size-1500 fraction), 568 nm (size-500 fraction), and 300 nm (size-300 fraction). With increasing MMT concentrations, horizontal ARG transfer was initially enhanced and then became inhibited at transition concentrations of 0.100 g/L for the size-1500 fraction, 0.050 g/L for the size-500 fraction, and 0.025 g/L for the size-300 fraction (Figure 1). The smaller MMT size fractions had a stronger effect on horizontal ARG transfer. At lower MMT concentrations, horizontal ARG transfer was enhanced by an increased level of plasmid−cell contact and possible hole formation in the cell membrane, whereas at higher MMT concentrations, it was inhibited by binding of the plasmid to MMTs and its aggregation facilitated by released metal cations (Figure 2). Our results provided new insight into the influence of clay minerals on ARG transfer in soils, thus improving our understanding of the environmental fate of ARGs.

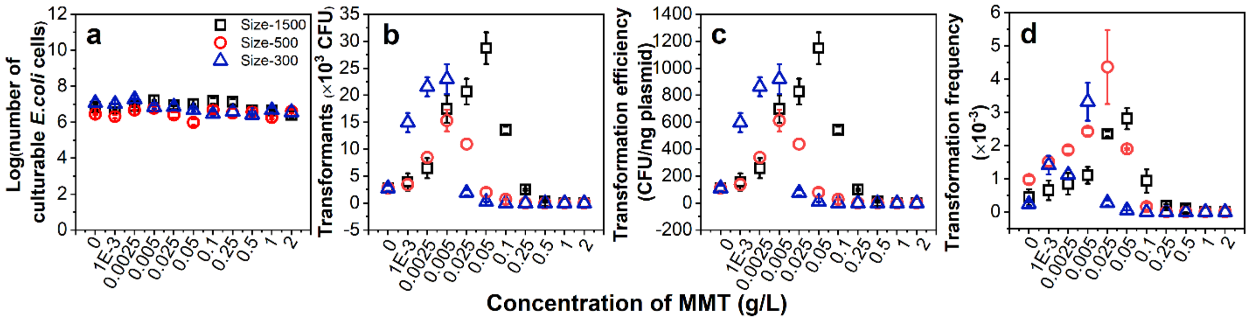

Figure 1: Effect of different size fractions of montmorillonites (MMTs) on the horizontal transfer of antibiotic resistance genes (ARGs): (a) culturable E. coli cells in the presence of MMTs, (b) number of transformants, (c) transformation efficiency, and (d) transformation frequency.

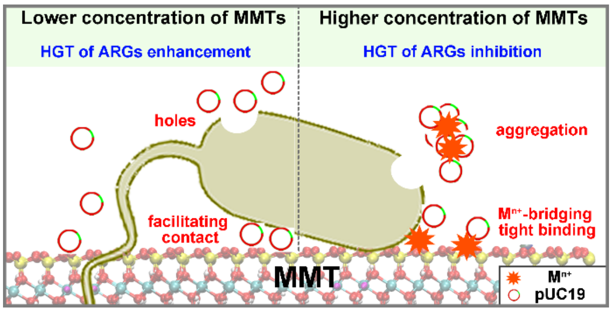

Figure 2: The influential mechanisms of MMTs on the horizontal transfer of ARGs

Molecular-scale Understanding of Sulfate Exchange from Schwertmanniteby Chromate versus Arsenate

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Schwertmannite effectively sorbs chromate (Cr(VI)), yet the sorption mechanisms remain elusive. We determined the Cr(VI) sorption mechanisms on schwertmannite at pH 3.2 and 5 using combined macroscopic sorption experiments with molecular-scale characterization and by comparing to arsenate (As(V)) sorption. Cr(VI) adsorbs as bidentate-binuclear (BB) inner-sphere complexes through exchanging more sulfate and less >Fe-OH/OH_2, with 0.59 - 0.71 sulfate released per Cr(VI) sorbed. While As(V) also forms BB complexes, it exchanges sulfate and >Fe-OH/OH_2 equally with 0.49 - 0.52 sulfate released per As(V) sorbed. At high loadings, As(V) precipitates as amorphous $FeAsO_4$, particularly at low pH. The above differences between Cr(VI) and As(V) can be related to their different ionic radii and binding strength. Moreover, Cr(VI) and As(V) preferentially exchange sulfate inner-sphere complexes, increasing the proportion of sulfate outer-sphere complexes in schwertmannite. In turn, the concentration of sulfate outer-sphere complexes increases and then decreases with increasing Cr(VI) loading. Results suggest that an oxyanion, which would form inner-sphere complexes on a mineral surface, preferentially exchanges inner-spherically bound oxyanions than outer-spherically bound ones on the surface despite both are exchanged. This study improves our understanding of sorption of oxyanions on schwertmannite and their capabilities to template schwertmannite formation and stabilize its structure.

PL2

Arsenic mobilization and removal – causes and solutions for the World's largest mass poisoning

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Contamination of groundwater and drinking water with the toxic metalloid arsenic is a global threat to humans. Various biogeochemical processes have been made responsible for causing the arsenic water contamination, including competitive sorption/desorption with other ions (e.g. phosphate), complexation of As ions by natural organic matter, and arsenic redox transformation by abiotic and biotic processes (Muehe et al., 2014; Zhu et al., 2017; Shi et al., 2020). In particular microbial reduction and dissolution of As-bearing Fe(III) oxyhydroxide minerals is considered to be one key mechanism responsible for mobilization of arsenic from solids into groundwater (Glodowska et al., in press). However, in many cases the identity of the electron donor (typically organic carbon), is unknown. In this presentation I will show data from microcosm experiments using samples from a drilling campaign in an arsenic-contaminated groundwater system in the village VanPhuc, in the Hanoi area (Vietnam). I will first discuss to which extent older natural organic matter that is already present in the subsurface (e.g. from old peat lenses) or methane formed by methanogenic microorganisms are serving as electron donor for microbial Fe(III) mineral reduction and As mobilization (Glodowska et al., 2021a and 2020b). In the second part I will show how household sand filters (containing raw sand from the Red River) are used for removal of arsenic and iron from the groundwater (Voegelin et al., 2014). I will discuss how a combination of microbial and geochemical processes lead to the formation of poorly crystalline Fe(III) oxyhydroxide minerals on the sand and how these minerals sequester and therefore remove the arsenic from the water (Nitzsche et al., 2015a and 2015b). Finally, I will discuss the short-term and long-term filter performance.

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Oceanic (Ba, Sr)SO_4 mysteries and aquatic Sr removal: Heterogeneous (Ba, Sr)SO_4 nucleation on organics

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Due to the much higher solubility of $SrSO_4$ than $BaSO_4$, Sr-rich marine barite ($BaSO_4$) formation in undersaturated seawater is paradoxical, and Sr removal from produced water of hydraulic fracking through coprecipitation with barite as (Ba, Sr)SO_4 is problematic. Here we report the promoted Sr-rich (i.e, high x value) $(Ba_xSr_{1-x})SO_4$ formation on mixed thiol (-SH) and carboxyl (-COOH) coated SiO_2 from understaturated bulk solution. Real-time observation of $(Ba_xSr_{1-x})SO_4$ initial nucleation kinetics reveals that small (Ba_xSr_{1-x}) SO_4 nuclei (~ 2-4 nm) kept formation at water-organic interfaces; while big (~ 5 µm) crystals formed in bulk solution. The enrichment of cation ions (e.g. Ba^{2+} and Sr^{2+}) at the organic-water interfaces were measured, which could lead to much higher supersaturation in the local solution at organic-water interfaces. The high supersaturation promoted heterogeneous $(Ba_xSr_{1-x})SO_4$ nucleation on the organics. The precipitates in bulk solution were Ba-dominant ($x \approx 1$), which was consistent with thermodynamic predictions of solid solution growth .While the $(Ba_xSr_{1-x})SO_4$ precipitates at organic-water interfaces were Sr enriched (1-x = 0.28-0.93), which was attributed to a lower interfacial energy of $SrSO_4$ (0.097 J/m^2) over $BaSO_4$ (0.125 J/m^2). The measured x values were consistent with calculations of solid solution nucleation rates. This study provided valuable insights for uncovering the mysteries of Sr-rich marine barite formation in oceans, as well as for the removal of aquatic Sr through coprecipitation with barite.

KN6

Coupled Kinetics of Arsenic Adsorption/Desorption and Redox Reactions at the Mineral-Water Interfaces

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Understanding the kinetics of coupled reactions of arsenic (As) at the mineral-water interfaces (e.g., adsorption/desorption and redox reactions) is crucial for predicting the dynamic behavior of As in the environment. In natural environments, manganese (Mn) oxides exhibit high oxidation ability with As, thus affecting As speciation and distribution. Furthermore, As fate and transport are usually coupled with iron (Fe) oxide transformation and mediated by both abiotic reactions and microbial processes in the environment. Currently, there is still a lack of mechanistic and quantitative understanding on the coupled reactions in controlling the kinetic behavior of As at the mineral-water interfaces, which was complicated by the heterogeneity of mineral binding sites, coupling of multiple reactions, and temporal changes of microbial functions.

In this talk, we will first describe the development of the coupled kinetics model for As adsorption, desorption, and oxidation reactions at the Mn oxide-water interfaces [1], in which we were able to simultaneously compute the adsorption/desorption rates of both As(III) and As(V) with time during the As(III) oxidation process. We also quantified the temporal changes of As(III) oxidation rates on Mn oxides, which were highly dependent on As loadings on Mn oxides. Then we will focus on our recent work on quantifying the microbially mediated kinetics of ferrihydrite transformation and As reduction reactions [2, 3]. We developed a kinetics model for multiple coupled processes, including microbially mediated As adsorption/desorption, time-dependent microbial reduction linked with the As(V)-reducing gene expression, transformation of Fe oxides, and structure incorporation of As into Fe oxides. Our model highlighted the importance of microbially induced As(V) desorption for controlling the As(V) reduction in Fe mineral-As-microbe systems. We also found that the temporal changes of microbial reduction rates were highly correlated with the As(V)-reducing gene expression patterns, which may provide a way to integrate the microbial functions into the kinetics model. Using the quantitative model developed, we further assessed the kinetic coupling of the microbial reduction and chemical reactions, which controlled the dynamic behavior of As species.

Overall, our research contributes to developing comprehensive models for predicting the kinetic behavior of metals/metalloids in soil environments by coupling other chemical, physical, and microbial processes. At the end of the talk, we will discuss the frontiers and major challenges on quantifying the multi-scale kinetic processes in soils, which is essential for predicting the fate of contaminants and elemental cycling in the environment.

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Environmental implications of humic acid and Fe oxides nanoparticle interaction

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Humic acid (HA), a naturally occurring and widely distributed natural soil organic matter (SOM), is one of the most important soil component controlling the transport and fate of toxic substance in soil environment. Goethite, hematite and magnetite nanoparticle strongly interact with HA and contribute to the transport of several pollulant in soils. Particle size is a key factor to understand the interaction between HA and Fe-oxides, and therefore the spectroscopyc techniques are the main tools that help to elucidate this feature. Fe oxides such as magnetite, maghemite, hematite and goethite can be efficiently identified by its intrinsic magnetic properties, complemented with other more usual techniques as X-ray diffraction, ultraviolet-infrared or FTIR spectroscopy. Fe oxides nanoparticle are used for carbon sequestration and for water cleanup. In particular Fe-oxides nanoparticles has an important influence on the stabilizzation of organic matter. Because of the low Fe concentration in soil and the natural SOM variability the research has led into the identification of labile pools of organic matter or small organic molecules with high iron affinity (e.g. phytosiderophores, siderophores, phenolics, and carboxylic acids) that are more active to form stable complexes. The presence of HA may promote the solubility of Fe, presumably by supplying soluble complexing agents that interfere with Fe cristallization. Adsorption/ Aggregation and transport of toxic molecules depend on surface charge of Fe oxides nanoparticle and chemical parameters such as pH, ionic strength, and humic substance composition. Humic acid (HA) contains versatile functional groups, such as carboxylic acid, phenol hydroxyl, alcohol hydroxyl, ketone, quinone and ester groups. There are three possible interactions between HA, heavy metal ions and Fe oxides nanoparticles. The first is a complexation between HA and the Fe ions; the second involves the electrostatic interactions between the acidic functional groups of HA and the goethite/hematite surface and finally the coprecipitation. Coprecipitate HA-Fe oxides are widely used for adsorptive/separative removal form water of dyes, arsenic, phosphate, molybdate, fluoride, selenium, Cr(VI), Cd(II), Cu(II), Pb(II), radionuclides, and organic pollulant. For example Arsenite/Arsenate retention is mainly attributed to co-precipitation within magnetite and/or adsorption on hematite, goethite and ferrihydrite. The small size and high surface area of magnetite nanoparticles make them and ideal adsorbent. Surface area of magnetic nanoparticles plays a significant role in the adsorption process. SEM, AFM and FTIR indicate that Fe oxides nanoparticles are produced as coatings on fine sediments with irregular morphology. These features allow HA-Fe oxides coprecipitate to be very usefull for a long-term remedial option for contaminated aquifers by phosphate, arsenic, borate and fluoride. Biogenic magnetite could be regenerated by Fe(II) produced by microorganisms after their oxidation by chlorinated solvents. Thus, abiotic degradation by biogenic Fe oxides may be long lasting if reducing conditions are maintained. This relationship can be used to design “in situ permeable reactive barriers” systems. Important attention sould be paid also to the application of hematite nanoparticle in the natural attenuation of contaminants in soil and for water treatment. The development of a low-cost, fast, and large-scale process for the synthesis of Fe oxides nanoparticle is essential for incorporating materials with diverse environmental applications. Green synthesis is an area in need of further investigation becouse more economical raw materials may be exploited for decontamination purpose.

KN8

Redox reactivity of manganese oxides versus inorganic contaminants: Beneficial role of associated (in)organic ligands

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In addition to the sorption reactivity related to their nanocrystalline character, Mn oxides are known as active redox species leading, through surface reactions, to the oxidation of redox sensitive contaminants including organic and inorganic molecules and elements (As, Co, Cr). This dual reactivity is of special interest for water treatment. The progress and efficiency of these redox reactions, enhanced by the possible coexistence of heterovalent Mn cations, is often limited however by the precipitation of low valence Mn (hydr)oxides and/or of iron (hydr)oxides at the surface of pristine Mn oxides, leading to their passivation [1].

The presence of (in)organic chelating agents in solution may alleviate surface passivation or even enhance redox reaction progress, depending on the affinity of chelating agents for low valence Mn species [2]. The coexistence of Mn oxides and (in)organic molecules in suspension may also trigger and/or kinetically favor involved redox reactions.

The present presentation will illustrate some of these remarkable modifications of Mn oxides redox activity versus inorganic contaminants (As, Co, Cr) in the presence of (in)organic molecules chelating Mn species. To this purpose, solution chemistry and crystal chemistry of the common Mn oxides involved will be followed as a function of reaction progress paying special attention to the evolution of Mn and contaminant oxidation states. Reaction mechanisms will be deciphered from the evolution of these chemical and structural parameters.

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Oral 9

Iron oxide surfaces against chromate pollution

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The environmental and health risks associated with chromate ions in aqueous and soils systems are related to its chemical speciation and interactions at the solid-solution interface. Thus, the presence of nanosize colloidal particles in these systems controls the transport, distribution and bioavailability of chromate. Among these colloidal particles, amorphous iron (hydr)oxides, due to its high specific surface area and high density of reactive sites, play a major role as a chromate scavenger and determine the fate of this ion in the environment. Ferrihydrite and schwertmannite can be selected as proxy of amorphous iron (hydr)oxide minerals usually present in systems affected by acid mine drainage (AMD).

In the present work, we study the binding of chromate ions on ferrihydrite and schwertmannite surfaces at macroscopic and microscopic scale. Adsorption of chromate on these mineral surfaces was evaluated as a function of pH, ionic strength and in the presence of major competing ions from AMD systems, i.e. sulphate. The results revealed that increasing the pH or the sulphate concentration favours the mobility of chromate ions (Figure 1a), which can be attributed to the changes on the surface charge, to the sulphate-chromate competition for common binding sites, and to the decrease of anion-exhange reactions. The macroscopic observations were then simulated with surface complexation models, specifically with the CD model. The selection of chromate and sulphate surface complexes were constrained by spectroscopic information. In the case of chromate, monodentate and bidentate inner-sphere complexes were selected, while in the case of sulphate monodentate inner-sphere and bidentate outer-sphere complexes were needed.

Once the chromate adsorption process was evaluated, we studied the thermodynamic stability of the mineral phases at variable Cr/Fe ratio, pH and temperature. The incorporation of chromate at the mineral surface or within the crystalline structure increased the mineral stability, while incresing the pH or temperature of the systems promote the transformation to pseudo-crystalline iron phases, e.g. goethite or hematite (Figure 1b). The transformation products were characterized by solid-phase techniques, e.g. XAS, XRD, SEM, TGA and ATR-FTIR. Finally, the remobilization or redistribution of chromate and changes in the reactivity of the mineral phases formed was evaluated.

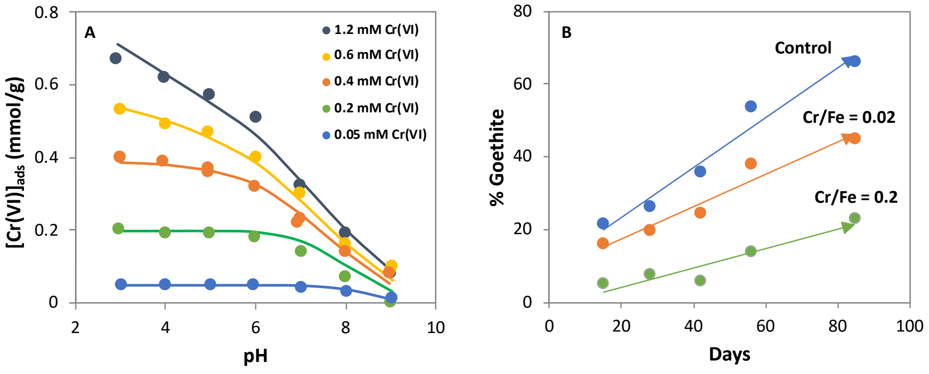

Figure 1:** **A) Effect of pH on the adsorption of Cr(VI). Symbols and lines correspond to experimental and CD model predictions, respectively. B) Fraction of goethite formed as a function of time at variable Cr/Fe molar ratios

Oral 10

The conditional affinity spectrum, a tool for the interpretation of adsorption data and adsorption isotherms

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The description of equilibrium binding data of cations to macromolecular ligands or surfaces has attracted the attention of many researchers due to its relevance in many fields. To gain knowledge on the physical characteristics of the ligand, a simple strategy is based on assuming that the ligand contains a continuous or discrete set of sites with different affinities, so that the binding can be described as a superposition of independent binding to each kind of sites. Fitting the set of sites and abundancies yields the affinity spectrum (AS). A direct numerical fitting of the binding data is an ill-defined process, so that regularization needs to be incorporated as a way to stabilize the AS. Alternatively, the binding data can be fitted to an analytical isotherm which in many cases, is a phenomenological expression. The underlying affinity spectrum can, then, be obtained as an analytical expression as reported by Sips. Extension of this process to the description of competitive binding can be done with the so called Conditional Affinity Spectrum (CAS), based on keeping constant all concentrations except that of the target binding cation.

Among the isotherms reported in the literature, the NICA model [1] has received great attention from the community, due to its simplicity and the ability to fit binding data of metal cations to humic and fulvic substances as well as to surfaces [2]. By incorporating the Donnan model to account for the electrostatic effects, NICA leads to physical parameters that characterize the intrinsic properties of the ligand, independently of the composition (pH, ionic strength and concentration of competing binding agents) of the medium.

Assuming langmuirian binding to all the sites, a simple analytical expression associated to the CAS of the NICA isotherm (CAS-L) was reported [3]. The change of the CAS-L as a function of pH or ionic strength, described with simple analytical expressions, allows an easy physical rationalization of the binding properties of the ligand or surface [4].

Using a local Hill isotherm in the splitting of the global binding seems an interesting alternative to the Langmuirian one, to explicitly consider the possible formation of chelates or other non-ideal phenomena between the cation and the functional groups of the ligand. In this contribution, the CAS underlying the NICA isotherm using a local Langmuir-Freundlich binding will be reported (CAS-LF) and compared to the CAS-L. Moreover, the dependence of the CAS-LF on pH and other parameters is extremely useful to clarify the evolution of the occupied sites, the average affinity of the empty sites or the conditional heterogeneity with the concentration of the binding agent, pH or other conditions.

Other competitive isotherms can also be analysed in this framework. A global critical discussion of the results of this work allows to evidence strong and weak points in describing the binding data with a given isotherm.

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Oral 11

The photocatalytic reduction of U(VI) over CdS/g-C_3N_4

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The photocatalysis can be used as an effective strategy for separating aqueous uranium. However, the low reaction efficiency of the photocatalytic system in open air strongly restrained its practical application. In this study, CdS/g-C_3N_4 nanocomposites were developed for reducing U(VI) under visible-light. Remarkably high photocatalytic efficiency was realized without the aid of any electron sacrifice, where uranyl was reduced to U(IV) only within 6 min, being the fastest among the ever-reported researches. CdS/CN-33 showed an optimal reaction rate of 0.641 min^{-1}, being 9.67 and 64.10 times of that for pristine CdS and g-C_3N_4, respectively. Most importantly, a satisfying performance was achieved for the photocatalytic U(VI) reduction in open air, as well as under solar irradiation and a 4 W LED lamp. The extraction capacity for uranium reached 2,379 mg/g, and the recycled CdS/g-C_3N_4 nanocomposites could keep high stability and activity.

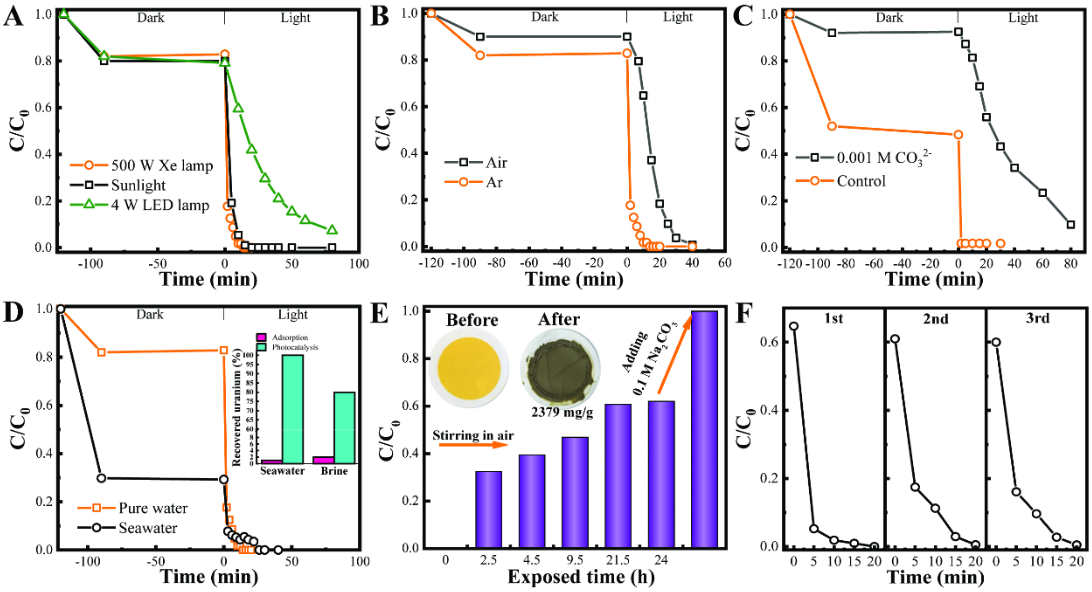

Fig. 1 The photocatalytic reduction of U(VI) on CdS/CN-50 under various light sources (A); Comparison of the photocatalytic U(VI) reduction performance in air and Ar atmosphere by CdS/CN-50 (B); The photocatalytic reduction of U(VI) in the presence of carbonate, pH = 8.0 (C); The photocatalytic reduction of U(VI) in U(VI)-spiked seawater and pure water, [U(VI)] = 0.1 mmol/L, Ar atmosphere. The insert shows the adsorption of U(VI) and the photocatalytic U(VI) reduction in seawater containing 1.0 μmol/L U(VI) and saline brine containing 0.1 mmol/L U(VI) in open air (D); The elution of photo-induced uranium deposits, and the inserts depict the color of CdS/g-C_3N_4 composite before and after the photocatalytic reduction of U(VI) (E); The cycling tests of photocatalytic U(VI) removal from aqueous solution over CdS/CN-33 (F).

Oral 12

Addressing the electrostatic component of protons binding to humic matter beyond the approximate Donnan level: theory and application to analysis of proton titration data.

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Chemical and electrostatic descriptors of humic matter nanoparticles (HNPs) are currently evaluated from proton titration curves measured at various solution ionic strengths and analysed by NICA-Donnan (NICAD) modelling framework[1]. However, the interfacial electrostatic representation adopted in this Donnan-based model,and in others like WHAM, suffer from well recognized approximations regarding the way the electrostatic potential is distributed within the particle body and in the neighbouring electrolyte solution.It has been recently demonstrated that the Donnan model violates the fundamental Poisson-Boltzmann (PB) equation when applied to HNPs with size comparable to Debye layer thickness under practical salinity conditions (1 mM-100 mM)[2].

Accordingly, we recently reported[3] a physically sound PB-based alternative to rationalize the necessarily coupled electrostatic and chemical contributions to proton binding on soft HNPs that are permeable to ions from the background electrolyte. The theory integrates the non-linearity of the PB formalism applied to soft surface electrostatics, which allows treatment of weakly to highly charged nanoparticles representative of natural organic matter.

The electrostatic and chemical parameters were optimized to reproduce, concomitantly, raw proton titration data and associated proton affinity spectra measured at different salt concentrations by coupling a home-made Fortran program SPBT (**S**oft **P**oisson **B**oltzmann **T**heory) with **PEST** (Model-Independent Parameter Estimation and Uncertainty Analysis), an open-source software designed for the adjustment and estimation[4] of parameters upon confrontation of experimental data to predictive theoretical models.

The performance of the method has been illustrated for five HNPs of different origins, charges and sizes[3] as illustrated by **Figure 1** for the specific case of FPHA (Fully purified peat humic acid)[5]. The figure shows excellent agreement between titration data and SPBT-based theory for FPHA particles. In particular, the analysis reproduces with accuracy the electrostatic component of the proton binding to the particles, which is materialized by the correct positioning of the theoretical curves with varying background electrolyte concentration.

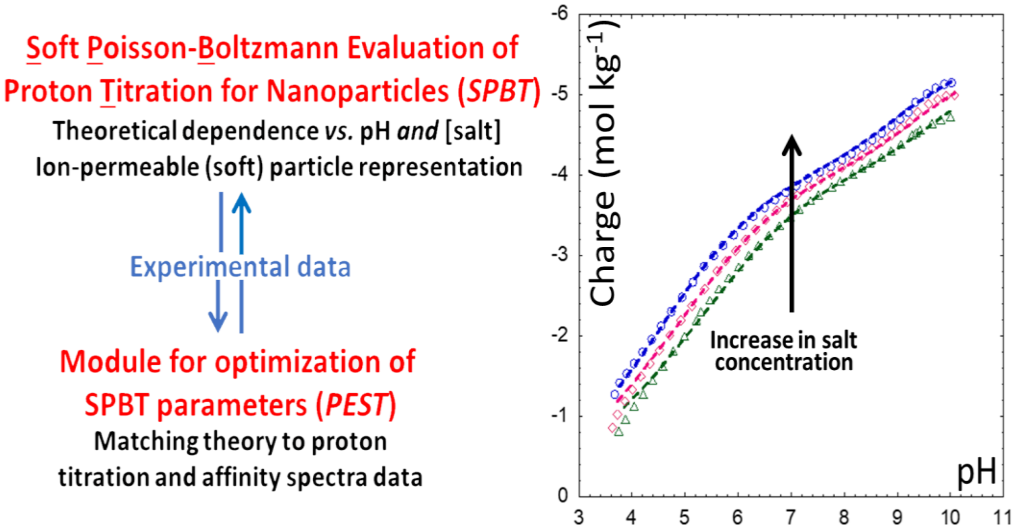

Figure 1: Scheme of the fitting procedure and proton titration curves measured for FPHA and collected at three NaNO$_3$ electrolyte concentrations: 10 mM (Δ), 30 mM (◊) and 100 mM (o). Symbols: measurements. Dotted lines: SPBT-PEST modelling results. The charge is expressed in moles of equivalent charges per kg of FPHA material.

Comparison[3] of the chemical parameters derived from our SPBT-PEST based procedure with those obtained via the NICA-Donnan model is detailed in

HNPs (*rp*, nm)	*Model*	Q_{maxH1} (mol kg-1)	log $\bar{K}_{a1}$	*mH1*	Q_{maxH2} (mol kg-1)	log $\bar{K}_{a2}$	*mH2*
FPHA (5.0)	SPBT-PEST	4.08 ± 0.02	4.26 ± 0.02	0.46 ± 0.01	1.39 ± 0.07	8.57 ± 0.09	0.59 ± 0.03
	NICA-Donnan(2)	3.18 ± 0.92	3.65 ± 0.23	0.66	3.02 ± 2.4	8.07 ± 0.77	0.29
SRFA (0.6)	SPBT-PEST	5.47 ± 0.06	3.20 ± 0.02	0.52 ± 0.01	1.0 ± 0.4	7.8 ± 0.2	0.5 ± 0.2
	NICA-Donnan(1)	5.55	3.01	0.42	NA*	NA*	NA*
LFA (3.6)	SPBT-PEST	3.79 ± 0.12	3.94 ± 0.03	0.52 ± 0.02	4.94 ± 0.10	8.5 ± 0.2	0.27 ± 0.01
	NICA-Donnan(1)	2.8 ± 1.2	2.5 ± 0.2	0.62 ± 0.17	7.4 ± 2.5	7.4 ± 0.7	0.18 ± 0.06
	NICA-Donnan(2)	5.1 ± 0.0	4.1 ± 0.1	0.41 ± 0.01	2.8 ± 0.0	8.6 ± 0.1	0.46 ± 0.02
Hf:FA (1.0)	SPBT-PEST	4.35 ± 0.09	3.81 ± 0.01	0.91 ± 0.02	1.75 ± 0.06	7.1 ± 0.3	0.33 ± 0.01
	NICA-Donnan(1)	5.0±0.01	2.29±0.01	0.44	0.94 ±0.03	6.85±0.02	0.59
Hf:HA (1.0)	SPBT-PEST	3.00 ± 0.05	4.40 ± 0.02	0.83 ± 0.03	1.3 ± 0.2	7.5 ± 0.2	0.49 ± 0.05
	NICA-Donnan(1)	3.44± 0.02	3.35 ± 0.01	0.46	0.64 ± 0.04	6.68 ± 0.03	0.88

Table 1:

HNPs (r_p, nm)	*Model*	Q_{maxH1} (mol kg^{-1})	log $\bar{K}_{a1}$	m_{H1}	Q_{maxH2} (mol kg^{-1})	log $\bar{K}_{a2}$	m_{H2}
FPHA (5.0)	SPBT-PEST	4.08 ± 0.02	4.26 ± 0.02	0.46 ± 0.01	1.39 ± 0.07	8.57 ± 0.09	0.59 ± 0.03
	NICA-Donnan(2)	3.18 ± 0.92	3.65 ± 0.23	0.66	3.02 ± 2.4	8.07 ± 0.77	0.29
SRFA (0.6)	SPBT-PEST	5.47 ± 0.06	3.20 ± 0.02	0.52 ± 0.01	1.0 ± 0.4	7.8 ± 0.2	0.5 ± 0.2
	NICA-Donnan(1)	5.55	3.01	0.42	NA*	NA*	NA*
LFA (3.6)	SPBT-PEST	3.79 ± 0.12	3.94 ± 0.03	0.52 ± 0.02	4.94 ± 0.10	8.5 ± 0.2	0.27 ± 0.01
	NICA-Donnan(1)	2.8 ± 1.2	2.5 ± 0.2	0.62 ± 0.17	7.4 ± 2.5	7.4 ± 0.7	0.18 ± 0.06
	NICA-Donnan(2)	5.1 ± 0.0	4.1 ± 0.1	0.41 ± 0.01	2.8 ± 0.0	8.6 ± 0.1	0.46 ± 0.02
Hf:FA (1.0)	SPBT-PEST	4.35 ± 0.09	3.81 ± 0.01	0.91 ± 0.02	1.75 ± 0.06	7.1 ± 0.3	0.33 ± 0.01
	NICA-Donnan(1)	5.0±0.01	2.29±0.01	0.44	0.94 ±0.03	6.85±0.02	0.59
Hf:HA (1.0)	SPBT-PEST	3.00 ± 0.05	4.40 ± 0.02	0.83 ± 0.03	1.3 ± 0.2	7.5 ± 0.2	0.49 ± 0.05
	NICA-Donnan(1)	3.44± 0.02	3.35 ± 0.01	0.46	0.64 ± 0.04	6.68 ± 0.03	0.88

Table 1: SPBT-PEST optimized values of the various chemical parameters involved in the Langmuir-Freundlich equation for the different HNPs types considered in our work.[3] (1) and (2) refer to the 1 and 2 parameters-dependent parameterisation of the Donnan volume introduced in NICA-Donnan model[6]. Indicated dispersions of the parameters correspond to the 95% confidence interval provided by PEST.

Table 1 shows that data reconstruction quality by NICA-Donnan for the largest FPHA and LFA HNPs considered in this work is quite comparable for all examined ionic strengths to that achieved by SPBT-PEST, whereas significant differences are observed for all other HNPs with lower particle radii. This conforms qualitatively with the fact that the a priori NICAD assumption of a constant intraparticulate potential is best verified for large particles, i.e., particles with size that well exceed the screening Debye length. Surprisingly, NICAD manages to provide a reasonable fitting of proton titration data for FPHA and LFA at low ionic strengths where Donnan criterion is not satisfied. This pure fitting end-result is however achieved at the cost of the physically unfounded introduction of a Donnan volume (V_D),[2,3] of its unrealistic adjustment with changing solution ionic strength and of fitted chemical parameters whose magnitude may amount to 100% compared to those derived on the basis of rigorous PB formalism.

Proton titration data modelling on the basis of the non-linear Poisson-Boltzmann framework for soft particle electrostatics describes properly the experimental data and avoids the requirement for the over-paremeterized NICA-Donnan model to adjust empirically any 'particle Donnan volume' found by NICAD to exceed the physical size of the particle, which is obvioulsy unrealistic.

The PB theoretical framework developed in this study can be extended to account explicitly for the presence of multivalent ions in solution and/or for any radial distribution (if required) of the particle structural charges. Both extensions of SPBT-PEST duo program are currently implemented in our group and they offer promising solutions for analysing the charging behaviour of heterogeneous (bio)particles in natural waters rich in metallic cations.

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AGNES and SSCP determination of free indium ion concentration

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Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) is a voltammetric speciation technique specifically designed to quantify free metal ion concentrations [1]. It has been applied to various amalgamating elements, amongst which indium has been recently tackled [2-4]. Despite the well-known irreversibility of the $In^{3+}/In°$ couple at the electrode surface, AGNES can have access to $[In^{3+}]$ because the timescale of the irreversibility is very short in comparison with the timescale of deposition until equilibration of the concentration profiles holding the Nernstian relationship [3]. Moreover, the fast interconversion of In^{3+} to indium hydroxides, which has been described as a reversible process [5], leads to equilibration times for $[In^{3+}]$ comparable to those needed for $[Zn^{2+}]$, $[Cd^{2+}]$ or $[Pb^{2+}]$. These theoretical considerations are consistent with the observed Nernstian proportionality between applied deposition potential and measured accumulated charge. Successful retrieval of $[In^{3+}]$ at various pH values and with ligands such as oxalate and NTA confirms the capability of AGNES beyond ions involved in fully reversible couples.

Scanned Stripping ChronoPotentiometry (SSCP) is a dynamic speciation technique, typically accessing to fluxes [6]. Under certain conditions, and with a suitable mathematical treatment, free concentrations can be also accessed from the full wave [7,8]. However, in most systems, there is an SSCP Nernstian region (roughly identified as the “foot of the wave”) where AGNES conditions apply and from which the free metal ion concentration can be retrieved. This AGNES-like region is clearly revealed with a new representation that will be discussed in the presentation. Again, indium irreversibility does not hinders Nernstian equilibration as checked with various strategies. One of this strategies shows how $[In(OH)_3]$ can also be found from AGNES or SSCP data.

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Oral 14

How to better explain ion specificity and competitive adsorption using calorimetric approaches

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Solid-liquid interfacial phenomena, involved in the industrial implementation of any separation or environmental technology, always occur under conditions of competition among the variety of ionic or molecular species present in the system, with possible specificity of adsorption. Despite efforts, thermodynamic studies of sorption of heavy metal cations or radionuclides rarely go beyond modeling sorption extent and rate, thereby leaving the thermodynamic models of the phenomenon essentially untested. The present study, undertaken to fill this gap, has been carried out with the aim of establishing the main driving force for heavy metal or radionuclides sorption, the effect of crucial physical factors governing the sorption mechanism, as well as under competitive conditions.

Liquid flow calorimetry was first applied to study the adsorption of several cations belonging to alkaline-earth and transition metal families on silica, at fixed pH, ionic strength, and degree of surface coverage [1]. All values for enthalpy of displacement ($\Delta_{dpl}h$) obtained in the present study were positive leading to the conclusion that displacement was an endothermic and entropy-driven process. For a given pH and surface coverage, the $\Delta_{dpl}h$ enthalpy was found to be linearly correlated with the molar enthalpy of cation dehydration in bulk water and to be much less sensitive to the specific (i.e., non-electrostatic) character of cation–surface interactions. The main hypothesis drawn from the comparative analysis of the calorimetric data was that the effects of cation dehydration upon adsorption, together with the deprotonation of surface silanols sites, contributed mostly to the pronounced endothermic character of the displacement process.

In a second stage, the use of nanoflower-like nanostructures was considered because of the potential impact of the layered structure on the retention performance [2]. These materials exhibited high retention capacity and good selectivity towards strontium when adsorbed from ultrapure water or multi-component solutions. Nevertheless, in the presence of calcium, some competition between the various cations was observed, which could be rationalized on the basis of the displacement enthalpies measured for the individual cations from single-solute solutions. Molecular simulations were performed to corroborate the conclusions drawn from the experimental studies. The competitivity between ions were explained using the Isotherm Titration Calorimetry (ITC).

In all cases, it was possible to shed more light on the retention mechanism and the pertinent physical factors governing it by combining the information obtained from the thermodynamic study of the sorption process underlying their retention performance, and especially direct calorimetric measurements.

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Proton binding to natural nano particles: specific and electrostatic interactions unravelled using charge density-pH curves

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To understand the ability of natural organic nano particles (NONP) to bind cations like metal ions and charged small organic molecules, the primary charge density due to dissociation of the functional groups as function of pH, Q(pH), should be known. The charging behavior is also important for the interaction of NONP with minerals and for their colloidal stability. The common experimental methods to obtain Q(pH) at constant 1:1 background electrolyte concentration (c_s) are potentiometric proton titrations and pH-stat titrations with 1:1-electrolyte. The functional groups of NNP are, in general, heterogeneous, and the effect of c_s indicates that electrostatic interactions play a role. Therefore, the degree of proton binding is determined by a total proton affinity distribution that is due to a *specific* (chemical) contribution, logK_H, and an *electrostatic* (Coulombic) contribution, logK_{el}, that is caused by the charge density of the NONP. For a detailed understanding of the proton binding the two components of the total affinity should be separated, but the two affinities cannot be measured separately. In literature, this is mostly solved by describing the specific binding with a proton binding equation that is extended with an electrical double layer (EDL) model that describes the electrostatic affinity [1]. However, simple EDL models may not be adequate for NONP and complex EDL models require particle properties that may not be available.These problems can be overcome by using an approximate experimental method that allows separation of specific and electrostatic affinities using the Q(pH) curves measured at different c_s. The basis of the method is the *condensation approximation* (CA). With the CA a Q(pH) curve (c_s=const) corresponds to the cumulative total affinity distribution $F_{CA}(\log K_t = \log K_H + \log K_{el})$. At high c_s, say 1M, the charges are screened and the electrostatic potential and logK_{el} go to zero, therefore logK_t = logK_H. At this condition the (extrapolated) Q(pH) curve reflects the specific proton affinity distribution and may be called the *Master Curve* (MC). The differences between the MC and the measured Q(pH) curves directly reflect the electrostatic contributions. In the presentation this will be worked out in more detail for humic-NP and discussed in relation to the Langmuir-Freundlich-Soft-Poisson-Boltzmann-theory [2] and the monocomponent NICA-Donnan model [1].

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Oral 16

Critical Role of Collector Surface Roughness on the Retention and Release of Nanoparticles in Porous Media

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The surface of natural porous media exhibits pronounced roughness and their physicochemical properties are highly influenced by soil colloids that are ubiquitous in the environment. The transport of nanoparticles (NPs) was greatly enhanced in relatively smooth sand in comparison to rougher sand, at higher pH, and lower ionic strength (IS). Additionally, complete release of the retained NPs was observed in smooth sand, while only limited release occurred for the rough sand. Differences in the surface roughness of the two sands which altered the energy barrier height and the depth of the primary minimum were the main cause. Limited numbers of NPs interacted in reversible, shallow primary minima on the smoother sand, which is consistent with the predicted influence of a small roughness fraction (e.g., pillar) on interaction energies. Conversely, larger numbers of NPs interacted in deeper primary minima on the rougher sand, which is consistent with the predicted influence at concave locations.

Natural soils have frequently been considered to decrease the mobility of NPs in comparison to quartz sand due to the presence of colloids that provide additional retention sites. In contrast, we demonstrated that the transport and release of NPs in sandy clay loam and loamy sand soils were enhanced in the presence of soil colloids that altered soil grain surface roughness. In particular, we found that the retention of NPs in purified soils (colloid-free and acid-treated) was more pronounced than in raw (untreated) soils or soils treated to remove organic matter. A significant number of concave locations on purified soils hindered NP release by diffusion or IS reduction due to deep primary energy minima. Conversely, NPs that were retained in soils in the presence of soil colloids were more susceptible to release under IS reduction because the primary minimum was shallow on the tops of convex locations created by attached soil colloids. Additionally, a considerable fraction of retained NPs in raw soil was released after cation exchange followed by IS reduction, while no release occurred for purified soil under the same conditions. Our work highlights the critical role of collector surface roughness and shows that the presence of soil colloids can inhibit deposition and facilitate the release and co-transport of NPs in soil by alteration of the soil grain surface morphology and shallow primary minimum interactions.

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Nanoparticle interaction with biological membranes: The role of proteins

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The cytoplasmic membrane represents the frontier between cells and their external environment and serves as an initial point of contact between nanoparticles and eukaryotic cells. Concerns about the interaction of engineered nanomaterials with biological systems in the environment have increased as their production and use has accelerated. Nanoparticle interaction with biological membranes is expected to be modulated by coatings of proteins acquired in biological fluids, as well as by peripheral and integral membrane proteins. This presentation will highlight our recent progress in understanding the roles of proteins in nanoparticle–membrane interactions. We find that the initial nanoparticle surface coating impacts the interactions with model cell membranes by determining the assemblage of complexing proteins, which in turn influences subsequent interaction with model biological membranes [1]. Using dissipative quartz crystal microbalance, nanoplasmonic sensing, and molecular dynamics simulations, we find that the peripheral membrane protein cytochrome *c* mediates membrane interaction of anionic nanoparticles which would not otherwise interact with the membrane [2]. Combining a mass spectrometry-based footprinting approach and computational molecular dynamics methods allowed the preferred nanoparticle-binding site on the protein to be ascertained [3]. Taken together, our results highlight the importance of the surface chemistry of both the nanoparticle and the membrane in predicting nano–bio interactions. We have further demonstrated that nanoparticles can perturb membrane protein function indirectly via changes in membrane properties [4].

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KN9

Molecular Geochemistry: Systematic understanding of behaviors of various elements and new methods to support the approach

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State-of-the-art spectroscopic methods on the chemical speciation developed in a recent quarter-century has provided various atomic-scale information even for trace elements in natural samples. The information includes oxidation state and local structural information of elements of interest, and interactions among atoms and molecules. This information in turn allows us to compare behaviors and cycles of various elements from chemical properties. Professor V. M. Goldschmidt defined that geochemistry is the study of the distribution and amounts of the chemical elements in minerals, rocks, soils, water, and the atmosphere, and the study of the circulation of the elements in nature *on the basis of the properties of their atoms and ions*.[1] In particular, systematic understanding of various elements based on physico-chemical information and periodic table is important. To achieve comparison of any elements in periodic table, speciation that can be applied to trace elements with high sensitivity is essential. For this purpose, X-ray absorption fine structure (XAFS) can be an ideal method, which consists of XANES and EXAFS, good tools to identify the oxidation state and local structure of the particular ion, respectively. If we could establish such systematic understanding based on such methods, we can predict behaviors of various elements based on the phsico-chemical laws. Thus, I here focus on (i) the systematic understanding of various elements (ions) in natural systems and (ii) new XAFS tools in terms of the sensitivity and information on the atomic scale interaction.

(i) Systematic understanding of various elements: One important process, which remains poorly understood, is adsorption of various ions on various adsorbents in water, which controls dissolved concentrations of ions and isotopic fractionation in water. For example, adsorption reactions on iron oxides and clay minerals are very different: the former is chemical interaction with hydroxyl group at the solid surface,[2] whereas the latter, in particular for smectites, is characterized by electrostatic interaction (except of the readion to the edge sites). Consequently, the stability of adsorbed species on iron oxides strongly depends on the ionic potential of each ion, whereas larger ions can be preferentially stabilized within the interlayer of smectites. These processes can explain retention of various toxic elements by the reaction in soils and sediments, enrichment of metal ions as resources and optimization of extraction procedure, and isotopic fractionation that can be geochemical tools. As for smectites, for example, caesium, or a largest cation, forms stable inner-sphere complex within the interlayer which makes it fixed at the surface of soil that contains smectites.[3] However, smaller ion that forms stable hydrated complex is adsorbed as outer-sphere complex within the interlayer that makes the ion readily exchanged with other cations in coexistent water.[4] This property makes clay minerals very effective mineral resources for rare earth elements (REE) called ion-adsorption type ore.[5] Here, the materials are same, but its macro-scale application is totally different that depends on the properties of elements, which can be systematically understood based on their ionic radii, or hard and soft acids and bases (HSAB) concept, or more quantitatively by nucleophilic constant (En)[6].

(ii) New XAFS tools: One important issue in (i) is the interaction of caesium ion with tetrahedral layer of clay minerals related to the formation of inner-sphere complex, since only the size (ionic radius) cannot be a cause for the formation of the inner-sphere complex. There should be some specific interaction between the cation and the tetrahedral layer, but such information cannot be given only by EXAFS, which only tells static structural information. For this purpose, XANES can be important, and a new technique using high energy resolution fluorescence X-ray detection system for XANES better than lifetime broadening effect (HERFD-XANES) has made XANES more important than before. For this purpose, the HERFD system using Bragg-type crystal analyzer (energy resolution better than 1-2 eV) is useful.[7] According to our recent studies using HERFD-XANES and its interpretation by hard and soft acids and bases (HSAB) concept, caesium has covalent-type interaction with tetrahedral layer to form stable inner-sphere complex for this soft cation. The HERFD system is also important to achieve sensitive analysis of XAFS for trace elements which can avoid interferences by fluorescence X-rays from other elements. For this purpose, a new detector, transition-edge sensor (TES), can be another powerful tool for fluorescence XAFS.[9] Various examples will be given in my presentation.

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KN10

Biofilm biology-informed biofilm engineering for environmental biotechnology

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Surface/interface-associated microbial communities, i.e., biofilms, represent the predominant mode of growth of microorganisms in natural, engineered and medical habitats. Compared with their planktonic counterparts, biofilms have been reported to be more tolerant to harsh physicochemical conditions. Microbial biofilms can be either beneficial or detrimental in different settings. The main research efforts in my group are focused on understanding biofilm-mediated environmental processes and applying the knowledge and insights of these processes to harness the power of beneficial biofilms and to combat detrimental biofilms in the context of environmental biotechnology. In this presentation, our recent work on the biofilm lifestyle of a model environmental bacterium and the biofilm biology-informed biofilm engineering enabled by multidisciplinary approaches will be discussed.

KN11

Humic acid-enhanced hydroxyl radical production during Fe(II)-bearing clay mineral oxygenation: Changes of electron transfer pathway and number

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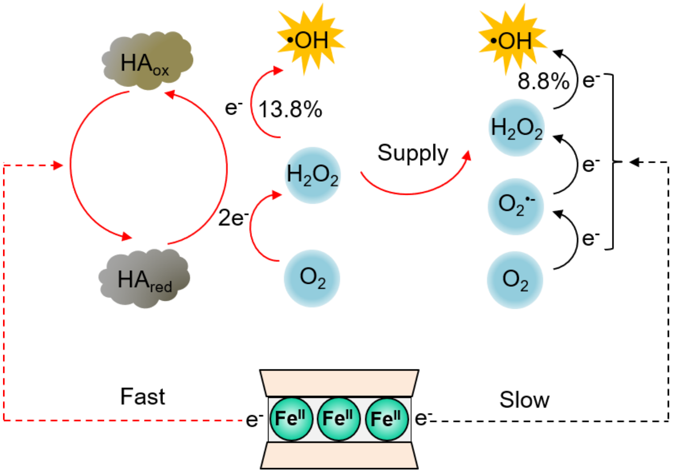
Hydroxyl radicals (•OH) production by electron transfer from Fe(II)-bearing clay minerals to oxygen has been increasingly reported. However, the influence of ubiquitous coexisting humic acid (HA) on this process is poorly understood. Here we investigated the effect of different HA on •OH production during oxygenation of reduced nontronite NAu-2 (rNAu-2), montmorillonite and a sediment. Results showed that HA could enhance •OH production, and the enhancement was related to the content of reactive Fe(II) in rNAu-2 and the electron accepting capacity of HA. Coexisting HA develops a new electron transfer pathway from Fe(II) in rNAu-2 to HA (instead of HA-Fe complex) and then to O_2, changing the first step of O_2 reduction from one- to two-electron transfer process with H_2O_2 as the main intermediate. Reduced HA decomposes H_2O_2 to •OH at a higher yield (13.8%) than rNAu-2 (8.8%). Modeling results reveal that HA-mediated electron transfer pathway contributes to 12.6%–70.1% of H2O2 generation and 13.2%–62.1% of •OH formation from H_2O_2 decomposition, with larger contributions at higher HA concentrations (5–100 mg C/L). Our findings implicate that HA-mediated electron transfer can expand the area of •OH production from mineral surface to aqueous phase and increase the yield of •OH production.



Acknowledgement (optional) - This work was supported by the National Natural Science Foundation of China (No. 41772374, 42025703, 41830862), the Natural Science Foundation of Hubei Province, China (2018CFA028), China Postdoctoral Science Foundation (No. 1232020), and the Program of State Administration of Foreign Experts Affairs & the Ministry of Education of China (B18049).

KN12

The spatiotemporal change of redox-sensitive elements in the soil-water interface and rice rhizosphere

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The chemical speciation and mobility of elements in soils are mainly controlled by the redox condition, pH, and organic matter content of the sediments. Under natural conditions, redox transition zones are often observed along the soil−water interface (SWI) and aquatic plant rhizosphere. In the zones, the biogeochemical characters vary at the mm scale. The element profile along SWI varies when the external environment changes (e.g., pH, seasonal wet−dry cycle, exogenous pollutants introduction, microbial degradation, and wetland plant roots activity). A deep understanding of the elemental behavior in the environment has been hindered to date by the techniques available to sample the zones.

In this study, a novel technique, called In-situ Porewater Iterative (IPI) sampler, was developed to map spatial and temporal distribution of elements along the typical micro-interfaces in flooded environments. The IPI sampler uses a single hollow fiber membrane tube for passive sampling and active sample injection, thus the workload for sample preparation is minimized. [1]

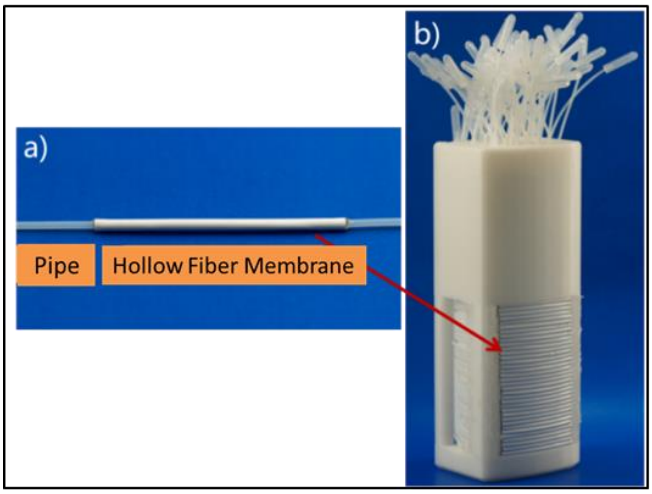

Figure 1: Schematic diagram of IPI sampler. a) a single sampler; b) the sample array for element profiling.

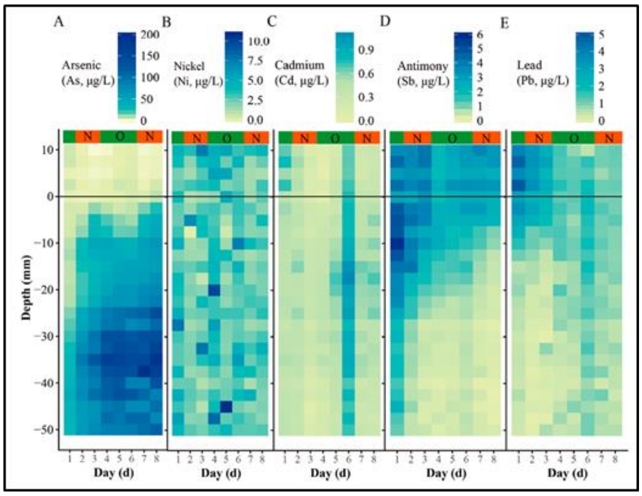

Figure 2: Dynamic vertical profile changes of As (A), Ni (B), Cd (C), Sb (D), and Pb (E) in paddy soil showed in heatmaps. "N" and "O" represent pumping N2 and air, respectively.

With the updated sampler, we reported the mm-scale mapping of Fe, As and other associated elements across the redox gradient in the SWI of five different paddy soils. The results showed a strong positive linear relationship between dissolved Fe, Mn, As, and P in 4 out of the 5 paddy soils, indicating the general coupling of these elements. However, decoupling of Fe, Mn and As was observed in one of the paddy soils.[2] Furthermore, the IPI sampler array (0-22 mm measurement distance in every 1.7 mm) was adopted to capture *in situ* tempo-spatial dynamics of ten elements (Fe, Mn, As, P, S, Cr, Co, Zn, Sb and Cd) in paddy rhizosphere to examine their covarying changes in time and space dimensions.

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Oral 17

The formation and application of free radicals on clay surfaces

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Clay minerals are important components in soil, and they are also influence the fate of contaminants in the environment. Recently, the development of electron paramagnetic resonance (EPR) provides us the opportunity to capture and identify the formed free radicals on clay surfaces, which should be closely related to contaminants' degradation, transformation and humidification.

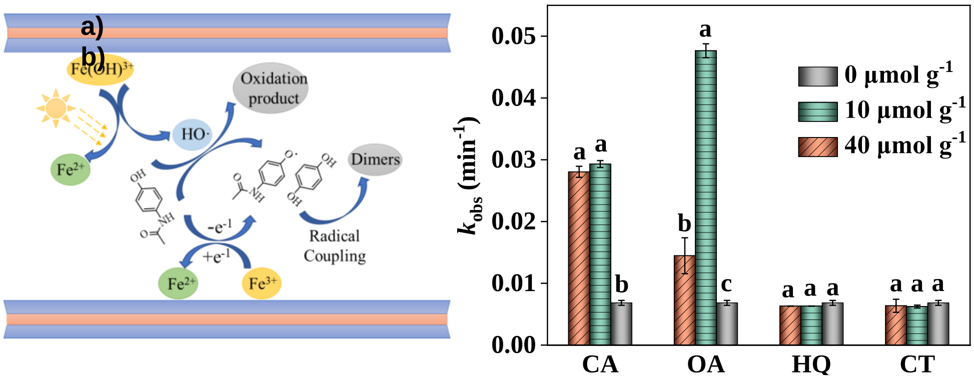

***Figure 1: a) The transformation pathways of acetaminophen with Fe-SMF; b)* The influence of organic compounds on ANT removal on *amophous silicates* under light.**

The studies in our lab found that Fe^{3+} saturated clay could not only induce acetaminophen (AP) to form AP• radical, then dimers, but also oxidate AP to form hydroxylated intermediate products (Figure 1a). Solution pH and dissovled oxygen could change the fraction distribution and valence status of iron species on clay surfaces, thus these two factors greatly impacted AP transformation and degradation; light irradaition could fasten electron transfer between AP and exchangeable Fe^{3+}. The formed organic acids from AP could further accelerate •OH formation and then AP degradation.

In reduced soil environment, clay minerals always exist as reduced clay-Fe(II), which could activiate peroxymonosulfate to form $SO_4^{\bullet -}$ radicals and •OH radicals, which could further degrade adsorbed organic contaminants, such as PAHs. Soil organic material always bounds to clay surfaces and form persistent free radicals (PFRs). In another study, we mixed catechol and hydroquinone with amophous silicates, and irradiated the mixture under simulated sun light for 5 min, strong PFRs signals were detected, which were close related with relative humidity, organic concentration and oxygen levels. These PFRs could react with adsorbed PAHs, for example anthracene (ANT), and form dimers. The presence of catechol and hydroquinone could slow down ANT removal due to the competition for reactive sites. However, the presence of oxalic acid and citric acid could accelerate ANT removel due to produce more •OH (Figure 1b).

In summary, soil clay minerals play the important roles in the removal of organic pollutans, and soil organic matter, clay types and environmental factors (such as humidity, sunshine, oxygen and solution pH, *etc*.) can significantly change their degradation kinetics, transformation pathways and transport ability.

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Oral 18

Aggregation of microplastic particles in the presence of humic acid: Effects of KCl and CaCl$_2$ solutions

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The world waterways are polluted by plastics and microplastic particles day by day. This plastic load in water bodies is an alarming issue now. Considering the transport and fate of microplastics, we studied the aggregation, charging, and aggregate strength of polyethylene microsphere (PEM) particles in the presence of natural organic matter (NOM) as a function of KCl and CaCl$_2$ concentration. The electrophoretic mobility of PEM particles in the presence of Suwannee river humic acid (SRHA) was negative in the investigated concentration range of KCl and CaCl$_2$ solutions. The formation of large aggregates was confirmed using microscopic observations. The aggregate strength of PEM particles was investigated using a laminar converging flow. The maximum aggregate strength was found around 1.87 nN in the presence of 100 mg/L SRHA at 0.5 M CaCl$_2$ solution. The higher aggregate strength of PEM particles in the CaCl$_2$ solution than that of KCl solution indicates the more effective bridging flocculation and divalent bridging due to the Ca^{2+} ions (Figure 1 A, B).

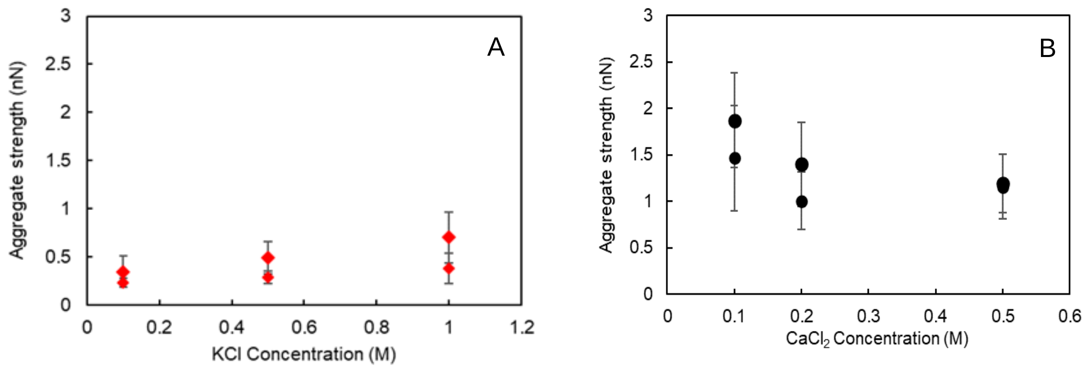

Figure 1. Aggregate strength of polyethylene microsphere (PEM) particles in the presence of 1000 mg/L of PEM and 100 mg/L of Suwannee river humic acid (SRHA) in KCl (A) and CaCl$_2$ (B) solutions.

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Oral 19

Simultaneous quantification effects of pH, calcium and phosphorus on the adsorption of arsenic in Paddy Soils

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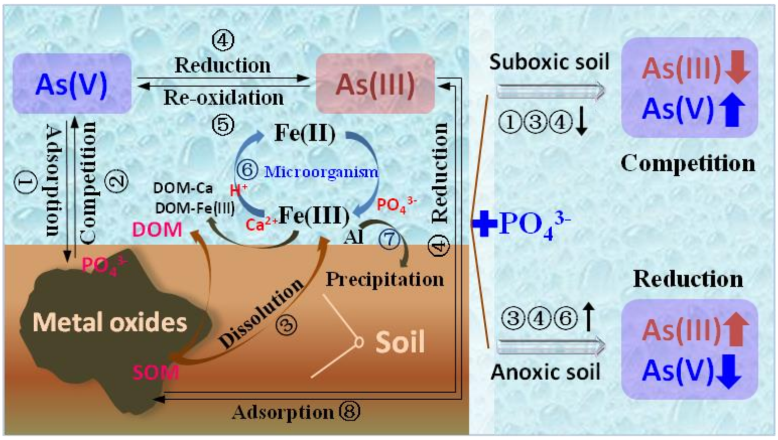
Contamination of arsenic (As) in paddy soils has drawn much attention in the past decades. Phosphate based fertilizers are commonly used in paddy field. Elevating speciation and distribution of As is essential to assess the risk of As in paddy soils. In this study, effects of phosphate on speciation of As in six paddy soils differing in redox status were studied over a range of pH (pH 3-9) and different background calcium (Ca) levels by batch adsorption experiments, by combing the Ligand and Charge Distribution (LCD) and Natural Organic Matter-Charge Distribution (NOM-CD) model to reveal the influence mechanisms. Results showed that the two models can describe effects of pH, calcium and phosphate on As speciation in these paddy soils. Contrasting effects of phosphate on As speciation were observed in the suboxic and anoxic soil. Under suboxic conditions, phosphate inhibited Fe and As reduction probably due to stabilization of Fe-(hydr)oxides, but increased soluble arsenate concentration as a result of competitive adsorption between arsenate and phosphate. In an anoxic soil, phosphate stimulated Fe and As reduction and caused increases of arsenite in soil solution under both acidic and neutral/alkaline pH. The understanding obtained in this work can be used in future to explain and predict the environmental process of anionic pollutants such as arsenate, arsenite and phosphate in paddy fields as well as in natural soil/sediment-water systems.



Mechanistic understanding about Fe(II)-catalyzed ferrihydrite transformation

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Fe(II)-catalyzed ferrihydrite (Fh) transformation into more stable Fe-(oxyhydr)oxide is ubiquitous in natural soils, waters, sediments, and acid mine drainage environments, playing critical roles in contaminants mobilization, nutrients cycling, and anaerobic microbial metabolism. In order to further understand the mechanisms of Fe(II)-catalyzed Fh transformation at the molecular level, we isolated and quantified a critical labile Fe(III) species by using a selective Fe(III) reagent, and revealed its production from Fe(II) oxidation on Fh surface[1]. The transformation process in the catalysis of Fe(II) now can be known as the accelerated Fe(III) olation and oxolation reactions to nucleate and sustain growth of secondary minerals by high reactive intermediate labile Fe(III). Moreover, on the basis of intermediate labile Fe(III) analysis, it was clarified that citrate, as a surrogate for natural dissolved organic matters, significantly impacts Fh transformation primarily through its ability to complex labile Fe(III) and thereby disrupt polymerization into product crystallites, as opposed to modifying the surface properties of Fh or inhibiting Fe(II)-Fh interactions[2]. Our insights into the molecular mechanism of ferrihydrite transformation have the potential to help a better understanding on the environmental behaviours of ferrihydrite and the fate of concomitant contaminants in natural systems.

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Oral 21

Manganese oxide-coated zeolite decreases the Cd uptake of wheat plants in Cd-contaminated weakly alkaline farmland soils

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Cadmium pollution in farmland soils has posed serious threats to food safety and human health. Manganese oxide minerals have been widely applied to the removal of heavy metals for their high adsorption capacity, especially in alkaline environments. However, the performance and stability of manganese oxides and the underlying mechanism of cadmium immobilization in dry farmland soils remain unclear. In this study, manganese oxide-coated zeolite was prepared and used for the immobilization of bioavailable cadmium in weakly alkaline soils (pH 7.89 ± 0.09) of wheat field. The cadmium bioavailability in soil was significantly reduced by a maximum of 44.3% due to the transformation of exchangeable cadmium to more stable Fe-Mn oxide-bound cadmium in the presence of manganese oxide-coated zeolite. The manganese oxide-coated zeolite could effectively decrease the relative content of soil available Cd by transforming exchangeable Cd to Fe-Mn oxide-bound Cd in weakly alkaline soils. In the presence of the manganese oxide-coated zeolite, the contents of soil available Cd and exchangeable Cd could be significantly decreased, and the content of Fe-Mn oxide-bound Cd was significantly increased by a maximum of 36.8%. The Cd immobilization efficiency increased with increasing manganese oxide content in the passivators. The corresponding Cd content in wheat grains was significantly decreased by 66.4%, which could be mainly attributed to the decrease of available Cd and increase of available Mn in the soil. The manganese oxide-coated zeolite also showed excellent chemical stability and Cd immobilization efficiency in weakly alkaline soils for a two successive year of pot experiment. These findings indicate that manganese oxide-coated zeolite is promising for the remediation of Cd-contaminated weakly alkaline farmland soils.

Acknowledgements

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Electron transfer at the interface between *Shewanella*, pyrogenic carbon and nitroaromatic compounds.

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Biogeochemical redox reactions play an important role in the formation and dissolution of minerals and organic matters in soils and, consequently, control the retention and release of trace elements associated with these minerals and organic matters [1]. Electroactive microorganisms, like *Shewanella,* are capable of extracellularly respiring on minerals and organic matters, and take part in lots of biogeochemical redox reactions. To accomplish this, *Shewanella* strains usually metabolize substrates to generate electrons and transport them to the outer surface of the membrane by using electron-transfer proteins located on the outer membrane [2]. Some natural organic matters, such as pyrogenic carbons and humic substances, can mediate electron transfer at the interface between microbes and acceptors, thus accelerating the biochemical transformation [1] (Figure 1). Nowadays, extracellular electron transfer (EET) has been a hot topic in the world. However, natural organic matters mediated EET between electroactive microorganism and polutants remains poorly elucidated.

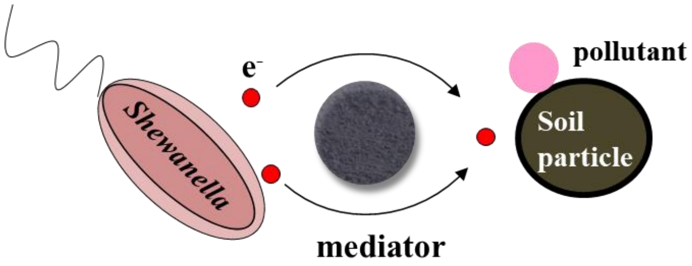

Figure 1: EET between Shewanella and pollutants.

In the precent study, we studied the reduction of nitroaromatic compounds by *Shewanella oneidens*is MR-1 with using of pyrogenic carbon as mediator. We found that nitroaromatic compounds differed in structure were reduced via different electron transport pathways on the membrane. The reduction of nitrobenzene, 4-nitrotoluene, 4-ethylnitrobenzene, 1-tert-butyl-4-nitrobenzene, 1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene and 2,4,6-trinitrotoluene occured via both the Mtr respiratory pathway and NfnB related pathway. However, 2,5-ditertbutyl-nitrobenzene, 2-nitrobiphenyl and 2,2’-dinitrobiphenyl were reduced only via the Mtr respiratory pathway. When pyrogenic carbon was added the system, some nitrobenzene was sorbed onto the pyrogenic carbon. Pyrogenic carbon slightly facilitated the reduction of nitrobenzene in both the liquid and sorbed phases by *S. oneidensis* MR-1. Anthraquinone groups in the pyrogenic carbon were deemed as the most likely oxygenated functional redox compounds on the basis of both voltammetric curve tests and spectroscopic analysis. The findings of the study provide valuable insight on the mechanism for pyrogenic carbon-mediated EET and the alleviation of pollution of nitroaromatic compounds in soils.

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Oral 23

Iron-montmorillonite-cyclodextrin composites as recyclable sorbent-catalysts for the adsorption and surface oxidation of per-fluorinated compounds.

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Iron-clay-cyclodextrin composites were designed to adsorb and oxidize per-fluorinated compounds from water. Seven perfluorinated compounds (PFAS and PFOS), ranging in chain size from C_4 to C_{10}, were chosen to test the efficiency of the novel materials. Clay montmorillonite decorated with nanoparticles of iron oxides served as a Fenton-like catalyst, and the cyclodextrin molecules cross-linked with polyfluorinated aromatic molecules were used to accommodate adsorption of the pollutants and accelerate oxidation. The FeOx-clay surface was synthesized and characterized in terms of size, morphology, and activation properties. The nano-sized oxides were amorphous with both di- and tri-valent iron present, and the oxidant activation properties were significantly higher than magnetite and nano-magnetite decorated clays [1,2]. The resulting iron-clay-β-cyclodextrin-polymer composites exhibited excellent adsorption of the long-chained PFAS (C_7-C_{10}). PFOA, for example, was completely adsorbed under the tested conditions - showing affinity to the βCD- polymer, not the iron-clay surface. To accommodate adsorption of the lower chained PFAS, the composites were further optimized in terms of cyclodextrin size and charge. PFAS degradation using H_2O_2 was followed by TOC, LC-MS and ICP. Degradation efficiency was inversely correlated to the chain length - meaning high MW PFAS were less prone to degradation at the adsorbed state. Still, PFOA (C8) degradation was highly efficient, reaching over 80% removal after one hour. Moreover, in the presence of other micropollutants (atrazine and bisphenol A) - a selectivity towards the per-fluorinated compounds was observed [3]. In addition, the composites' activity remained steady for five consecutive cycles with negligible damage to the materials - highlighting their durability and applicability. The ability to remediate a broad range of per-fluorinated pollutants, and the high overall removal exhibited by these novel materials, demonstrates the potential for future application in water remediation technologies.

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Highly enhanced As(III) oxidation at the surface of birnessite in the presence of pyrophosphate: depassivation effect & reaction mechanisms

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Manganese(IV) oxides, and more especially birnessite, rank among the most efficient metal oxides for As(III) oxidation and subsequent sorption, and thus is a potentially attractive oxidant to be used in large-scale treatment for arsenic immobilization. The efficiency is limited, however, by the precipitation of low valence Mn (hydr)oxides at the birnessite surface that leads to its passivation. Moreover, the aqueous Fe(II), presenting in anaerobic water, also reacts on the MnO_2 mineral surface, resulting in formation of hydrous ferric oxides and inhibiting As(III) oxidation. The present work investigates experimentally the influence of chelating agents on this oxidative process. The precipitation of Mn(III) and Fe(III) on the surface of birnessite will be removed in the presence of pyrophosphate (PP), an efficient Mn(III) chelating agent, thus alleviating surface passivation and highly promoting As(III) oxidation. Enhancement of As(III) oxidation by Mn oxides strongly depends on the affinity of the chelating agent for Mn(III) and from the induced stability of Mn(III) complexes. Compared to PP, the positive influence of oxalate, for example, on the oxidative process is more limited. The present study thus provides new insights into the possible optimization of arsenic removal from water using Mn oxides, and on the possible environmental control of arsenic contamination by these ubiquitous non-toxic mineral species.

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PL4

Machine Learning Exploration of Biochar Amendment in the Immobilization of Soil Heavy Metals

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The application of biochar to contaminated soils is a promising strategy for both sustainable waste management and green remediation. Remediation of heavy metal (HM) contaminated soil by biochar primarily depends on a number of properties of the soil, biochar, and HM. The determination of the optimum conditions for HM immobilization in biochar amended soils is site-specific and variable among different studies. Thus, a generalized approach capable of predicting the HM immobilization efficiency in biochar amended soils is required. Here, we employed machine learning (ML) approaches for systematically mapping the HM immobilization efficiency in biochar-amended soils, based on four main empirical categories including experimental conditions, biochar, soil, and HM properties. We found that the N content in the biochar (within 0.3-25.9 N% range) and the biochar application rate (within 0.5-10% range) were the two most significant features for HM immobilization. Causal analytics revealed the important empirical categories for HM immobilization efficiency, in the order of biochar properties > experimental conditions > soil properties > HM properties. Our study presents new insights on understanding the effect of biochar characteristics and soil properties for HM immobilization while enabling the identification of optimum conditions for enhanced HM immobilization in biochar amended soils. This work was supported by the Cooperative Research Program for Agriculture Science and Technology Development (Project No. PJ01475801), Rural Development Administration, Republic of Korea. This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1A2C2011734).

Nanoparticles and the Mineral/Biofilm/Solution Interface

KN13

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Over the last decades, the important increase in nanoparticles (NPs) production and use resulted in their release in the environment and raise important concerns regarding their potential to negatively impact ecosystems. In the environment, NPs are likely accumulated in soil where it is expected that they will interact with bacterial biofilm/mineral interfaces, one of the most reactive compartments (figure 1) [1]. This complex interface exhibits highly specific physico-chemical properties that can control NPs fate and transformations (dissolution, aggregation...). In this presentation we will address the partitioning of NPs at this interface, the transformations that NPs can undergo and to physico-chemical parameters that control NPs behavior. To do so, Shewanella oneidensis MR-1 biofilms were grown on oriented single crystals a-Al2O3 (1-102) and were exposed to silver nanoparticles and Quantum Dots. NPs partitioning and stability were mostly investigated using Long Period – X-ray Standing Waves – Fluorescence Yield spectroscopy and Grazing Incidence – X-ray Absorption Spectroscopy.

This work allows to demonstrate that NPs partitioning at the interface is mostly controlled by the mineral surface. Nevertheless, biofilm is able to slow down NPs migration depending on NPs size and aggregation state, NPs surface charge and coating type ((in)organic, hydrophobic properties). When NPs migrate through biofilm thickness, they undergo transformation, and more specifically dissolution. This dissolution is partly controlled by microenvironments within biofilm thickness but also by the presence of thiol groups at EPS and cells surfaces as well as in molecules secreted by bacteria.

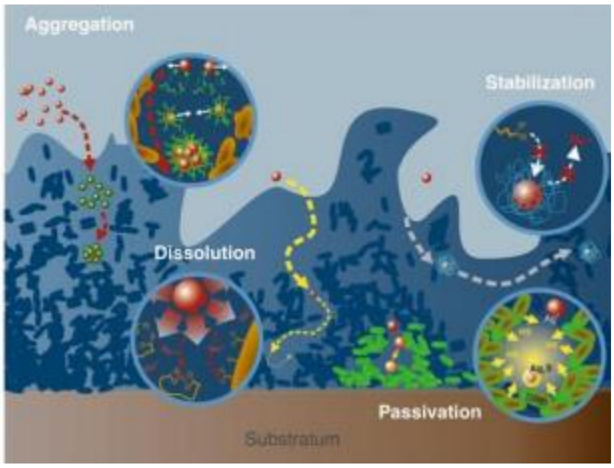

Figure 1: Potential nanoparticles transformations at the bacterial biofilm/mineral interface. Figure taken from [1]

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KN14

Flow Capacitive Deionisation (FCDI): does this interesting technology for water treatment and resource recovery have a future?

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Flow-electrode capacitive deionization (FCDI), a newly developed electrochemically driven ion removal approach combining ion-exchange membranes and flowable particle electrodes, has been actively explored over the past seven years, driven by the possibility of energy-efficient, sustainable and fully continuous production of high-quality fresh water, as well as flexible management of the particle electrodes and concentrate stream. In this presentation, I provide a brief overview of recent R&D at UNSW in areas relating to both contaminant removal and nutrient recovery [2, 3].

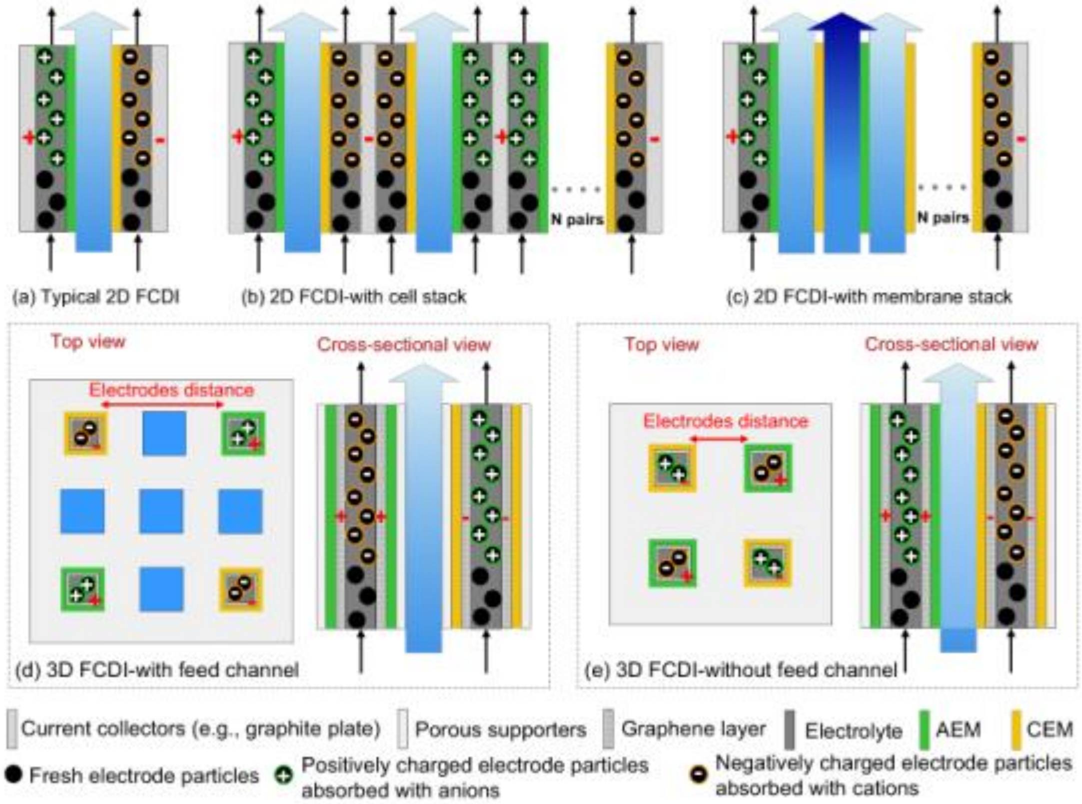

Figure 1: Schematic representation of various FCDI configurations: (a) typical 2D FCDI, (b) 2D FCDI with cell stack, (c) 2D FCDI with membrane stack, (d) 3D FCDI with additional feed channels and (e) 3D FCDI without feed channels (from [1]).

Particular attention is given to assessment of the most pressing challenges in achieving full scale application of this technology with presentation of recent efforts in scale-up by the UNSW team.

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Cotransport of plastic particles with different types of colloids in porous media

KN15

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The wide application of plastic products would inevitably release the plastics into the natural environment (Ivleva et al., 2017; Peixoto et al., 2019). It is expected that the amounts of plastics in environments would rise in near future, which would further enhance the concentrations of plastic particles in natural environments (van Wijnen et al., 2019). Noting that the potential environmental risks of plastic particles have correlation with their fate and distributions in natural environments, it is essential to understand the transport and deposition behaviors of plastic particles in porous media. Hence, we investigated the cotransport and deposition behaviors of iron oxides, clay particles, natural organic matters, TiO_2, graphene oxide, biochar, as well as bacteria with plastic particles (nanoplastic/microplastic) in porous media. We found that through different mechanisms, the copresence of natural colloids and engineering nanoparticles induced different effects on the transport and deposition behaviors of plastic particles in quartz sand. Likewise, via different mechanisms, different transport behaviors for natural colloid and engineering nanoparticles induced by the copresence of plastic particles were also observed. Clearly, due to the interaction with copresent colloids, the fate and transport/deposition of plastic particles in porous media would be changed. Therefore, to better predict the transport and deposition behaviors of plastic particles in porous media, the impacts of different types of colloids should be considered.

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KN16

Chemodynamic features of nanoparticles: insights into the dynamic life cycle of SARS-CoV-2

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The COVID-19 pandemic has sparked enormous international scientific efforts to understand the factors that determine the dispersal, transmission, and infectivity of the SARS-CoV-2 virion. Outbreaks of COVID-19 have been correlated with episodes of air pollution [1], and the potential for airborne transmission of COVID-19 is acknowledged [2]. These observations sparked our interest to explore the potential interactions between the virions and airborne particulate matter (PM). For this purpose, we have developed a generic chemodynamic framework for describing the physicochemical background of the virion's dynamic life cycle [3]. Our approach identifies the key physicochemical parameters that are fundamental for quantitative interpretation. A schematic overview of the involved processes is shown in Figure 1.

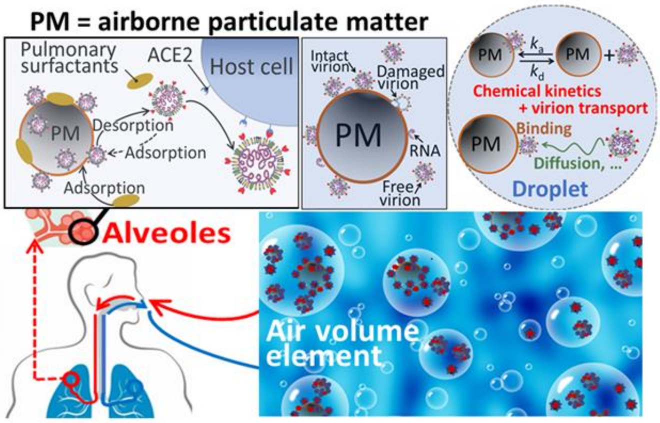

Figure 1: Schematic overview of the processes involved in the dynamic lifecycle of SARS-CoV-2 (taken from [3])

Our theoretical treatment assimilates the virion to a core-shell nanoparticle, and the contributions of various interaction energies to the virion-PM association (electrostatic, hydrophobic, London-van der Waals, etc.) are generically included. Despite the lack of quantitative data, our conceptual framework qualitatively predicts that virion-PM entities are largely able to maintain equilibrium with free virions on the timescale of their diffusion towards the host cell surface. Comparison of the relevant mass transport coefficients reveals that virion biointernalization demand by alveolar host cells may be greater than the diffusive supply. Under such conditions both the free and PM-sorbed virions may contribute to the transmitted dose. This result points to the potential for PM to serve as a shuttle for delivery of virions to host cell targets. Thus, our analysis reveals that the chemodynamics of virion-PM interactions may play a crucial role in the transmission of COVID-19, and provides a sound basis for explaining reported correlations between episodes of air pollution and outbreaks of COVID-19.

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Macroscopic screening of competitive and co-operative effects in selective retention of pollutant ions by charged solid surfaces

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Ionic pollutants discharged into aqueous streams as a consequence of anthropogenic activities may have a negative impact on the human health, because of their toxicity in living cells and the increased cancer risk. Azo dyes and heavy metals are a good illustration of the environmental issues. Heavy metal ions are usually ranked as the top listing on the Priority List of Hazardous Substances of the Agency for Toxic Substances and Disease Registry. In particular, the release to the environment, even at very low quantities, of such radionuclides as ^{137}*Cs,* ^{90}*Sr, or* ^{60}*Co greatly increases environmental and health risks. Another example refers to water pollution by textile industry, which is usually estimated to represent almost 20% of global industrial water pollution. Here numerous acid or basic dyes and fabric softeners are capable of dissolving in water to form ionised species. Adsorption at the Solid-Solution interface, and ion exchange in organic and inorganic solid exchangers in particular, is usually proposed as an important alternative to most existing technologies for* in situ *removal of pollutants from aqueous streams.*

The mechanism of adsorption from multicomponent ionic solutions at electrified interfaces has a strongly competitive character since the adsorption of the preferentially retained ionic species is accompanied by a variety of competing or co-operative effects, e.g., desorption of the pristine co-ions, surface dewetting, partial dehydration of adsorbed ions and rehydration of ions released from the interface to the aqueous solution. Changes in pH and ionic strength may additionally alter the adsorption mechanism and thus the structure of the ionic double layer surrounding the solid particles. It is for these reasons that the competitive effects do not show up clearly on adsorption isotherms. Measurements of the enthalpy changes accompanying competitive adsorption by means of isothermal titration calorimetry result in the so-called enthalpy of displacement as a function of the total amount of solutes adsorbed and provide a more precise account of competitive and co-operative effects involved in the adsorption mechanism. Further modelling of these enthalpy changes based on the principle of additivity of enthalpy contributions given individually by each solute component to the total displacement phenomenon allows the understanding of the adsorption mechanism to be improved. From the experimental point of view, this modelling approach requires two types of observables to be determined: (i) the individual adsorption isotherms for the solutes from multicomponent solution and (ii) the cumulative enthalpy of displacement curves for the solutes measured separately in single-solute solutions.

The validity of this modelling approach will be illustrated by the analysis of several bi-solute systems including either orange-type dye and inorganic anions (i.e., Methyl Orange, Orange II, Orange G, and chromate oxyanion) retained by strongly basic anion-exchange resin [1] or metal cations (i.e., Cd^{2+}, Sr^{2+}, Cs^{+}, Ba^{2+}, Ca^{2+}) adsorbed onto zeolites containing extraframework compensating cations [2]. The emphasis will be placed on such systems where the two solutes separately follow the opposite displacement patterns (i.e., exothermic and endothermic displacement). In an extension of this data processing to other types of adsorption system, an example of adsorption of Co^{2+} onto γ-alumina in the presence of acetate and citrate anions in aqueous solution will be considered to describe the co-operative effects leading to the formation of ternary complexes involving solid surface, as well as ligand and metal species [3].

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Study of glyphosate sorption onto chitosan molecularly imprinted polymers by surface plasmon resonance

Oral 26

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Nowadays, glyphosate, belonging to the herbicide family, is the most widely used compound in agriculture and urban settings1 in more than 130 countries. Its total global consumption is estimated at over 825 million kg2. Phosphonomethyl derivative of glycine3, this molecule is very polar, soluble in water (0.07 M at 25 °C) and insoluble in non-polar organic solvents4. Glyphosate behaves like zwitterion from pH 1 to 10 5. Under environmental conditions, glyphosate can be rapidly degraded to aminomethylphosphonic acid (AMPA), the main glyphosate metabolite6. Glyphosate can accumulate in the environment and aquatic systems but also migrate into soils and groundwater, to then be present as glyphosate residues in plant products7. Extensive evidence of human exposure to glyphosate has been reported8. The EU Water Framework Directive set a glyphosate standard of 0.1 µg/L (0.6 µM) in drinking water9.

The main objective of this study is to develop a retention method for this molecule in order to limit its propagation in the various environmental compartments. For this, an active layer made from a bio-sourced material, chitosan (CS), a linear cationic polysaccharide, was chosen10. This material, which is biodegradable, biocompatible, cheap, non-toxic, has good adsorption properties due to its amine and hydroxyl groups (wastewater treatment, selective separation, sensors)10, 11. Moreover, he has a good ability to form films. In this work, two techniques were compared for making chitosan molecular imprinted polymers: bulk imprinting12 and surface imprinting13. Crosslinking was necessary to stabilize CS and to control sorption and regeneration mechanisms. Two crosslinkers were used: epichlorohydrin (EPI) as crosslinker for OH groups of CS and glutaraldehyde (GA) as a reagent having primary amine functional groups14. The direct detection method used was based on the surface plasmon resonance.

In this presentation, we will on the hand show how a molecularly imprinted polymer (MIP) with the surface method obtained from chitosan showed real possibilities of sorption to selectively retain glyphosate, and on the other hand quantify sorption parameters from different sorption models such as the Langmuir-type one.

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Oral 27

Adsorption of cationic dyes onto unmodified and modified biochar

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The discharge of dye effluents poses a wide-spread threat to the environment, and adequate pre-treatment must be applied before these effluents reach aquatic systems. Carbon-based adsorbents such as activated carbons have been shown to efficiently remove cationic dyes from effluents, but, due to their high cost, these materials are not world widely implemented. In this study, we investigated biochars based on by-products of biorefinery industry as possible substitutes for activated carbons in methylene blue (MB) removal from aqueous solutions. In order to enhance the adsorption capacity of the biochar, surface modifications using NaOH and lignin were tested in terms of their physico-chemical characteristics and subsequent adsorbent properties. FTIR analysis confirmed the presence of aromatic rings and ether groups on raw biochar and NaOH-biochar, while in addition to these two former groups, carbonyl and carboxylic groups were identified for lignin-biochar. Thermogravimetric analyses showed one step of mass loss for raw biochar, and three steps of mass loss for lignin-biochar. This corresponds to the decomposition of cellulose materials, confirming intercalation of lignin inside the structure of biochar. Zeta potential measurements showed that raw biochar and NaOH-biochar presented a permanent negative surface charge across the whole pH range, whereas lignin-biochar exhibited a point of zero charge at pH = 2.

Adsorption experiments were performed as a function of time, pH, initial concentration of MB and in two different background electrolytes (NaNO3 and $CaCl_2$). The results showed that the adsorption equilibrium was reached after 60 min of contact time for raw biochar, lignin-biochar and NaOH-biochar. A pseudosecond order kinetic model was consistent with experimental data, compared to a pseudo-first order kinetic model. Adsorption of MB was highly dependent on pH for the three adsorbents. Increasing pH led to an increase in adsorption capacity. These results correspond with the permanent negative charge of the surface across the pH range, favoring MB adsorption via Coulombic attraction. Both the $NaNO_3$ and $CaCl_2$ background electrolytes exerted a negative effect on adsorption processes, and Ca^{2+} and Na+ acted as competitor ions and inhibited MB adsorption.

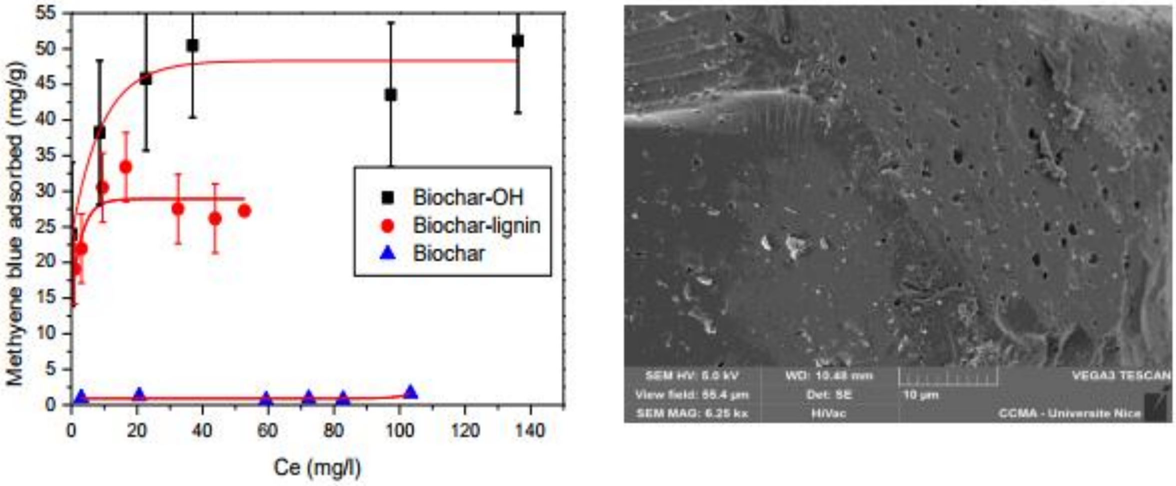

Figure 1: Adsorption isotherm curve of MB onto unmodified and modified biochar (a) and SEM image of NaOH biochar (b).

Adsorption isotherms as a function of initial MB concentration (Figure 1-a) show that adsorption of MB obeyed to the Langmuir model and NaOH-biochar exhibited the highest affinity towards MB when compared to raw biochar and lignin-biochar. According to these results, surface modification using lignin and NaOH strongly enhanced the adsorption capacity of biochar (25 times and 50 times, respectively). According to the SEM image (Figure 1-b), this increased adsorption capacity could be due to the formation of supplementary pores on the surface, resulting in an abundant mesoporous structure. Incorporation of lignin onto the biochar structure increased the oxygen-rich groups, thus providing supplementary reactive surface sites.

Oral 28

As(III) adsorption on Fe-Mn binary oxides: are Fe and Mn oxides synergistic or antagonistic for arsenic removal?

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Fe-Mn binary oxides are ubiquitous in the natural environment and have attracted increasing interest due to their high removal capacity for As(III), as well as their important role in the natural cycling of arsenic. Although numerous studies have characterized the respective roles of Fe and Mn oxides in As(III) removal, the working relationship between Fe and Mn oxides in different Fe-Mn binary oxides for As(III) removal has not been fully explored. In this study, three Fe-Mn binary oxides containing either ferrihydrite, hematite or goethite, were used to evaluate their adsorption capacities for As(III) in comparison with their corresponding single Fe and Mn oxide forms. The dynamics and speciation transformation of As(III) within mixed Fe and Mn oxides systems were investigated by using spectroscopic techniques of *in situ* flow ATR-FTIR and XPS combined with a Donnan reactor, where Fe and Mn oxides were isolated by a semi-permeable membrane through which arsenic could pass. The result showed that the synergistic effect, as well as antagonistic effects, between Fe and Mn oxides, was present in Fe-Mn binary oxides for As(III) removal. An obvious increase in As(III) removal by hematite containing Fe-Mn binary oxide, and a decrease by ferrihydrite containing Fe-Mn binary oxide, was attributed to As(III) oxidation mediated by Mn oxide as well as the difference in arsenic adsorption affinity in Fe oxides.

Activated carbon beads from chitosan for the NO_2 and formaldehyde removal from indoor air

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Nitrogen enriched Activated Carbons (ACs) were synthesized in form of beads and tested for the remediation of harmful indoor air pollutants such as nitrogen oxides or formaldehyde. Nitrogen enriched AC beads doped or not with Cu have been prepared by activation of chitosan hydrogel spheres with KOH or NH_3 (773-1173K) at various activating agent/chitosan impregnation ratios (m{activating agent}/m{chitosan}) in the range 20%-150%. The AC beads have been characterized by infrared spectroscopy, X-ray tomography, X-Ray Diffraction, Scanning Electron Microscopy (SEM), N_2 adsorption-desorption at 77K, CO_2 adsorption at 273 K, water vapour sorption at 298 K, X-ray Photoelectron Spectroscopy (XPS) and elemental analysis. The breakthrough curves of NO_2 and formaldehyde removal by the various ACs (20 mg amount) were studied at 850 ppb and 25°C, under 1.5 $L.s^{-1}$ air flow, in dry and humid conditions (20%-50% relative humidity) and correlated to their textural and surface-chemistry properties.

Regardless of the activating agent nature (KOH or NH_3), the porous volume showed a maximum at 63% impregnation ratio, at which microporous-mesoporous AC beads (about 2 mm diameter in Fig. 1a) possess the highest BET surface area (about 1000 m^2/g) and microporous volume ($\simeq$0.4 cm^3/g). The SEM and X-ray tomography images of these beads have revealed multi-scale porosities. The NH_3-activated beads are hydrophobic while the KOH-activated ones are hydrophilic and richer in oxygen. The NH_3-activated beads were found more efficient for formaldehyde adsorption and less effective for NO_2 removal than KOH-activated ones. This is related with a lower amount of oxygenated groups and higher amount of nitrogen groups such as pyridinic and pyrolic (evidenced by XPS) in NH_3 activated ACs (12 wt. %) compared to KOH-activated ones. The removal uptake capacities were found at about 100 mg/g and 60 mg/g for NO_2 and formaldehyde respectively.The latter is in agreement with previous works [1]. The formaldehyde adsorption competes with steam adsorption [2] while NO_2 removal is promoted by humidity through chemisorption reactions [3]. The presence of homogeneously dispersed Cu and copper oxide nanoparticles (Fig. 1b) in the AC beads obtained from Cu-doped chitosan was evidenced by SEM and XRD. For the Cu-doped AC beads, both for NO_2 and formaldehyde removal, a catalysis plateau was observed in the breakthrough curves showing on the one hand the possible catalytic reduction of NO_2 (maximum at 20% relative humidity) and on the other the formaldehyde decomposition in water and CO_2 (40% of the total removed formaldehyde).

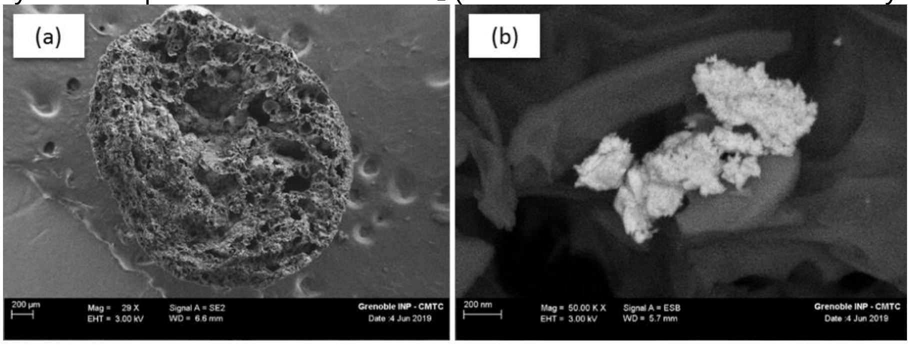

Figure 1: SEM images of KOH-activated carbon bead prepared from Cu doped chitosan at 63% impregnation ratio a) section obtained by cutting a bead with a scalpel; d) aggregate of copper nanoparticles.

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Oral 30

Hydration/Dehydration of adsorbed phthalic acid on goethite studied by IR spectroscopy and DFT+U Calculations

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The aim of the present study is to address issues about the chemistry of water unsaturated systems. When it comes to adsorption of molecules on solid materials, two types of systems have been studied: fully wet (aqueous/solid interfaces) [1] and fully dried (gas/solid interfaces) ones [2]; The phthalic acid/phthalate/goethite system has been investigated. Phthalic acid is known as a soil pollutant as well as a model Natural Organic Matter (NOM) chemical functionality [3]. Goethite is both a wellknown model to study soil adsorption reactivity and a solid used to test out adsorption models [4].

In this work, batch sorption experiments of phthalic acid on goethite were performed and deposits of the final suspension were dried in a humidity chamber. The samples were then analysed by IR transflection spectroscopy [5] while stepwise rewetting and dewetting the deposits. To support the experimental results and gain more detailed insights on what is happening at the surface, periodical ab initio calculations (DFT+U) [6]were made.

While analysing the system during the hydration/dehydration process, several behaviors were observed, depending on the thickness of the water layer above the substrate surface. The periodical DFT calculations are supporting the experimental results and give insights on the system while surface hydration increases, one water molecule after another.

Said behaviors were not all reversible upon dewetting, indicating that the changes are mainly of chemical nature and this study shows that the chemical nature of an adsorbed molecule may change depending on the water vapour content in the atmosphere.

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Are the binding groups of Baltic coastal dissolved organic matter affected by seasonal variabilities?

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The global carbon cycle supports current and future life on Earth, with dissolved organic matter (DOM) acting as a key bioactive carbon reservoir. Carbon cycle and thus climate, can be altered due to the mobilization of the DOM carbon pool, which depends on the DOM physicochemical characteristics, i.e. equilibrium binding constants, and heterogeneity [1].

Biogeochemical cycling in coastal margins is usually dominated by the influx of terrestrial organic matter and nutrients. Riverine, terrestrial and coastal DOM have been investigated over the last decades, although their role in nutrient binding, bioavailability, and transport of contaminants, is still unclear [2]. Some of the unanswered questions arise from the lack of a solid link between the sources and fate of DOM and its binding properties.

The main sources of Baltic DOM are primary production, terrestial/freshwater inputs and bio-phototransformation. Micronutrient and pollutant binding to organic matter occurs through complex interactions with many binding sites of variable strength and stoichiometry. Binding models that explicitly link metal complexation to the acid–base properties of organic matter and incorporate heterogeneous distributions of binding sites need therefore to be implemented [3].

Here we investigate the physicochemical properties of DOM extracted from surface waters that were collected at Boknis Eck (BE), a time series station located in the southwestern Baltic Sea. This area is characterized by the regular inflow of saline North Sea water through the Kattegat and the Great Belt, and the absence of riverine inputs. The research covers an annual cycle and hence, resolve potential seasonal variability. Our investigation provides binding properties of DOM with relevance for the transport, speciation, and bioavailability of nutrients and pollutants in coastal regions.

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Oral 32

Evolution of Ni crystal chemistry and stability in birnessite during aging at room temperature and treatment at different temperatures

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In terrestrial environments birnessite-like minerals play an important role in the fate and transport of heavy metal pollutants. Mineral transformations often change the metal mobility, however the effects of dry aging at room temperature for a long time and heating in air mimicking wildfires remain unknown. Here we first carefully checked the evolution of mineral structures of Ni-doped hexagonal birnessite during dry ageing at room temperatures for 5 and 8 years. Then the mineral transformation of the 8-year aged Ni-doped birnessite upon treatment at different temperatures ranging from 77-673 K and changes in the Ni crystal chemistry and stability were investigated. It demonstrates that, the birnessite mineral is much stable in a dry state at 298 K up to 8 years, with neither changes in the mineral phase purity nor structural characteristics such as Mn average oxidation state (AOS) and Ni ccordination environmengts. So is the treatment at low temperatures ranging from 77-323 K. Upon heating during 323-473 K, though birnessite keeps its layer structure, Ni^{2+} adsorbed on birnessite layer vacancies is gradually incorporated into the layers. A linearly positive relationship is observed between layer Ni fraction and temperature, implying the favorable migration of interlayer Ni^{2+} into layers during heating in this temperature range. Further increase in temperature (573-773 K) leads to the transformation of birnessite to cryptomelane with a sharp increase in Mn AOS. This greatly enhances Ni^{2+} stability in the minerals. Acid dissolution experiments show Ni release rate in the produced cryptomelane in 2 M HCl solution at 310 K is reduced by 396 ± 15 times compared to that in birnessite. After heating at 773 K for 2 h, birnessite with the highest Ni content (a Ni/Mn molar ratio of 0.13) is transformed to cryptomelane with a minor amount of $NiMnO_3$. Our study not only helps us to understand the stability of birnessilte-like minerals, but also reveals that thermal transformation of trace metal-containing birnessite-like minerals can greatly decrease metal mobility by driving the migration of interlayer cations into layers and mineral transformation.

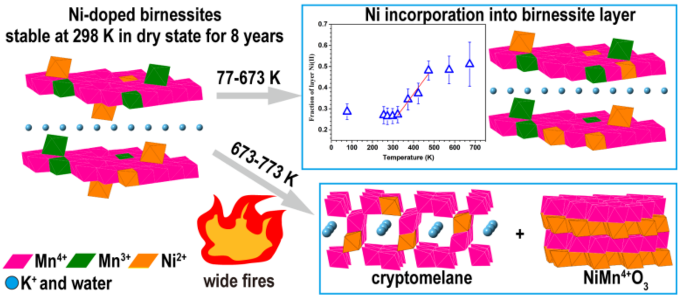

Figure 1: Effect of temperature on the transformation of birnessite-like minerals and the accompany evolution of Ni(II) crystal chemistry.

Oral 33

Natural organic matter-iron oxides interaction and effect on ion adsorption

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Natural organic matter (NOM), such as humic acid (HA) and fulvic acid (FA), bind very strongly to mineral surfaces such as the surface of iron oxides. The adsorption of NOM onto minerals is an important protection mechanism of organic carbon from degradation, and influences the distribution of many nutrients (e.g., PO_4^{3-}) and pollutants (e.g., AsO_4^{3-}) in the environment.
The Size Exclusion Chromatography (SEC) and Nuclear Magnetic Resonance (^{13}C NMR) results suggested that, due to the polydispersity of HA and FA, preferences of certain fractions took place during their interaction with iron oxides and the preference depends on the loading and pH [1, 2]. Both HA and FA have a strong competition effect on oxyanion adsorption to iron oxides, and the strength of the competition effect depends on the charge and particle size of NOM. NOM-CD model and LCD model are advanced surface complexation models that can describe anion adsorption to oxides in the presence of NOM. The LCD model helped us to quantitatively describe and predict the adsorption of HA and FA to oxides [3, 4], and it was also used to account for the competitive or synergistic effects of NOM on the adsorption of Ca^{2+}, Cu^{2+}, PO_4^{3-}, AsO_4^{3} to oxides [5-8]. Attempts have also been made to apply the models to soil samples to reveal the amount of NOM in the Stern layer of soil minerals, and the distribution of PO_4^{3-} and AsO_4^{3-} as a function of e.g. pH [9-11].

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Oral 34

Effective heavy metal adsorption driven by electrochemically controlled redox of manganese oxides

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Heavy metal ions, the important chemical components in the wastewaters released from mining, extractive metallurgy and chemical manufacturing, increasingly threaten the ecosystem, agricultural production and human health. As one type of transition metal oxides, manganese oxides are widely used for heavy metal ion removal due to their characteristics of having low point of zero charge, abundant resources and being environmentally friendly. The adsorption capacities of manganese oxides for heavy metal ions are strongly affected by their properties including crystal structure, chemical composition and micromorphology. The chemical composition and micromorphology of manganese oxides can be adjusted by electrochemically controlled redox reactions. However, little is known about the effect of electrochemical redox reactions of manganese oxides on their heavy metal ion adsorption capacities. In this work, manganese oxides were used as adsorption materials. The electrochemical adsorption of Zn^{2+} and Cd^{2+} were conducted in a three-electrode system by multi-cycle galvanostatic charge−discharge based on the electrochemically-driven cyclic redox of manganese oxides (Figure 1). The highest removal capacities for Zn^{2+} and Cd^{2+} of birnessite reached 530.0 and 900.7 mg g^{-1}, whose were remarkably higher than the adsorption isotherm capacities of 56.1 and 125.8 mg g^{-1}, respectively. The improved adsorption capacity can be ascribed to the change in the crystal structure, chemical composition and micromorphology during dissolution-recrystallization process of manganese oxides. The electrochemical adsorption capacity of layer-structured birnessite is higher than that of tunnel-structured manganese oxides.

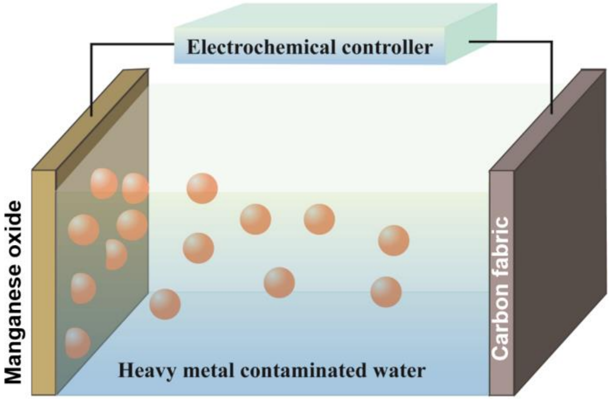

Figure 1: Schematic of the electrochemical system for heavy metal removal.

Table 1 shows the electrochemical removal capacities for heavy metal ions of different materials. The heavy metal ion removal capacities of birnessite electrodes obtained by the multi-cycle galvanostatic charge−discharge were higher than those of carbon materials and manganese oxide/carbon composite at a constant cell voltage.

Materials	Cell voltage (V)	Removal capacities (mmol kg^{-1})	References
Graphene nano-flakes	2.0	16.1 (Fe^{3+})	[1]
Modified activated carbon cloth	0.3	854.5 (Cu^{2+})	[2]
Activated carbon cloth	1.2	80.0 (Cd^{2+}), 107.5 (Pb^{2+})	[3]
MnO_2/Carbon fiber	0.8	2721.7 (Cu^{2+})	[4]
Birnessite	0-0.9 (*vs.* SCE)	8038.4 (Cd^{2+}), 8106.5 (Zn^{2+})	Present work

Table 2: Comparison of the ion removal capacities of deionization capacitors with different materials.

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KN17

Multimodal imaging of oil-in-water bilgewater emulsion and biofilms

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Bilgewater emulsions, consisting of oil and surfactant mixtures in water, affect many aquatic species. Thus development of methods and techniques to treat or mitigate the formation and undesired consequences of shipboard emulsions are urgently needed. This work presents new results of the evolution of the bilgewaer chemical and physical properties using in situ imaging. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model [1, 2]. Synthetic oil-in-water (O/W) emulsion droplets were seled in a vacuum compatible microfluidic sample holder and imaged using a suite of tools including scanning electron microscopy (SEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), confocal laser scanning microscopy, and optical microscopy, highlighting the advantage of multiscale analysis and its applications in waste reduction and treatment in the environment.

The transferrable and vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), was used in this study. SALVI enabled surface analysis of liquids and liquid-solid interactions using ToF-SIMS and SEM [3, 4]. Its detection window is an aperture of 2 μm in diameter open to vacuum, permitting direct detection of the liquid surface. Liquid is withheld by surface tension within the aperture. The interface is composed of a silicon nitride membrane and polydimethylsiloxane microchannel [3, 4]. A variety of samples including complex liquid mixtures, ionic liquids, single mammalian cells, live biofilms, and solid-electrolyte interface have been analyzed using in situ imaging [5, 6]. The feasibility of using SALVI for in situ SEM imaging of nanoparticles and colloids in liquid was recently demonstrated [7]. This paper shows new findings of multimodal imaging and analysis of synthesized emulsion particles in water. Figure 1 depicts a schematic of multimodal in situ imaging of bilgewater emulsion using SEM and ToF-SIMS.

Furthermore, we study the interactions of microbes and bilgewater emulsion. Microbes play an important role in the ocean. We hypothesize that microbes release organics that can act as surfactants that affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. *Pseudomonas* was selected as a model strain. Biofilms were cultured in a microchannel to allow culture [8]. Once a thick layer of biofilms was formed, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple in situ and ex situ techniques as described earlier. Our findings indicate that biofilms change the chemical makeup of the emulsion surface compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

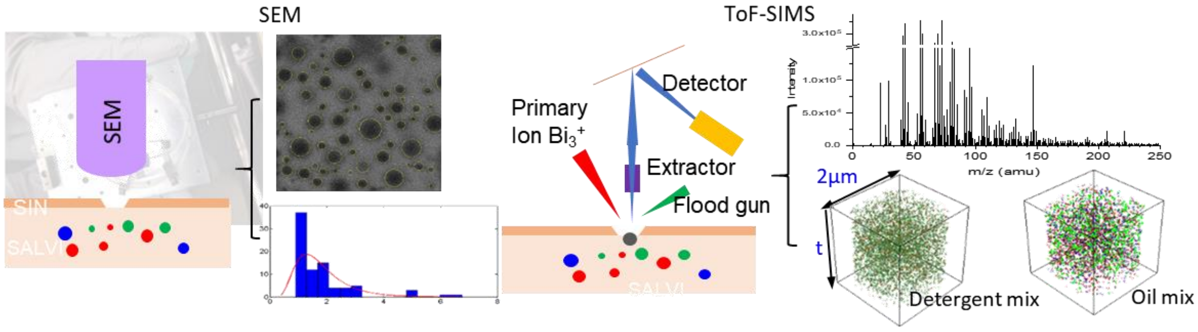

Figure 1: A schematic showing in situ multimodal imaging of bilgewater emulsion using SEM and ToF-SIMS

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KN18

Adsorption and oxidation of dissolved organic matter by iron and manganese oxides: Insights from ESI-FT-ICR mass spectrometry

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Interactions with mineral surfaces affect the composition and properties of dissolved organic matter (DOM) via adsorption-induced molecular fractionation and oxidation. While iron (Fe) oxides are well known to fractionate DOM, it remains unclear how surface chemistry of Fe oxides affect their fractionation capabilities. Much less is known for oxidation of DOM by manganese (Mn) oxides regarding compound selectivity and oxidative alteration of DOM. We quantified the degree of Suwannee River fulvic acid (SRFA) fractionation by adsorption on five iron oxide phases (ferrihydrite, goethite, Al-submitted goethite, hematite and Al-submitted hematite) under a wide range of DOM removal ratios, and oxidation of SRFA by δ-MnO_2 using electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). Result show that while the mineral phases and thus surface chemistry differ greatly, the fractionation powers of ferrihydrite and goethite are similar and slightly higher than that of hematite. The Al substitution changes the particle size and morphology, particularly for hematite, but not the fractionation power. The insensitivity of fractionation power to Fe oxide surface chemistry is attributed to organo-organic interactions that lead to multiple-layer adsorption. As to the Mn oxide system, we found that polycyclic aromatic hydrocarbons, polyphenols and carbohydrates are more reactive in reducing δ-MnO_2 than highly unsaturated and phenolic compounds (HuPh) and aliphatics, but highly abundant HuPh contributed the most (~ 50 %) to the overall reduction of δ-MnO_2. On average, oxidized species had higher molecular weights, aromaticity, carbon unsaturation degree, nominal oxidation state of carbon, and oxygen and nitrogen contents, but were lower in hydrogen content compared to unoxidized species. The oxidation decreased those molecular indices and oxygen and nitrogen contents but increased the hydrogen content, with stronger changes at lower pH. This DOM oxidation on polar mineral surfaces was more selective, but shared similar selectivity rules as adsorption. The abiotic oxidation resembles microbial oxidative degradation of organic matter, and Mn oxide-oxidizable carbon may be a useful index for detection and identification of dissolved labile organic carbon.

Structural design and interface regulation of graphene-based macromaterials for water purification

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Graphene-based macromaterials (GBMs) have extensive application prospects in water purification. However, the effective structural design and interface regulation of GBMs to improve their stability, selectivity and performance remain to be further studied. By using cysteamine as the covalent crosslinking agent, the interaction between graphene oxide (GO) can be effectively regulated. The porosity and mechanical strength of graphene/cysteamine composite aerogels are improved simultaneously. The composite aerogel can fully maintain its original morphology under strong acid and strong alkali conditions and exhibited superior oil adsorption performance. By using graphene nanosheets as the interface modification material, the wettability of different porous substrates can be effectively regulated, and the oil/water selectivity was significantly improved. The two-dimensional flexible wrinkle structure of graphene nanosheets makes it easy to modify the surface of porous substrate and form a variety of micro-nano scale rough structures. The hydrophobic reduced graphene oxide (rGO) can shelter the hydrophilic functional groups on the porous melamine foam (MF) substrate, and the surface energy was further reduced by the modification of octadecylamine (ODA). The obtained ODA-rGO@MF exhibited superhydrophobic/superoleophilic properties with a water contact angle of 153.5°. The hydrophilicity of GO and the cross-linking effect of Cu^{2+} endowed the modified GO@CuO mesh with stable superhydrophilic/ underwater superoleophobic. The GO@CuO mesh demonstrated excellent anti-oil-fouling property and its oil-water separation efficiency is up to 99.5%. To alleviate membrane fouling, A rGO/Ag@g-C_3N_4 membrane with photocatalytic self-cleaning performance was constructed by using Ag@g-C_3N_4 as intercalation material. The composite membrane exhibited excellent photocatalytic self-cleaning performance with a high flux recovery rate of 98.1%. The combination of high separation performance and photocatalytic self-cleaning ability makes the membrane have great potential for application in the practical water purification process.

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KN20

In-situ quick-scanning EXAFS measures rapid formation of surface precipitates at mineral-water interface

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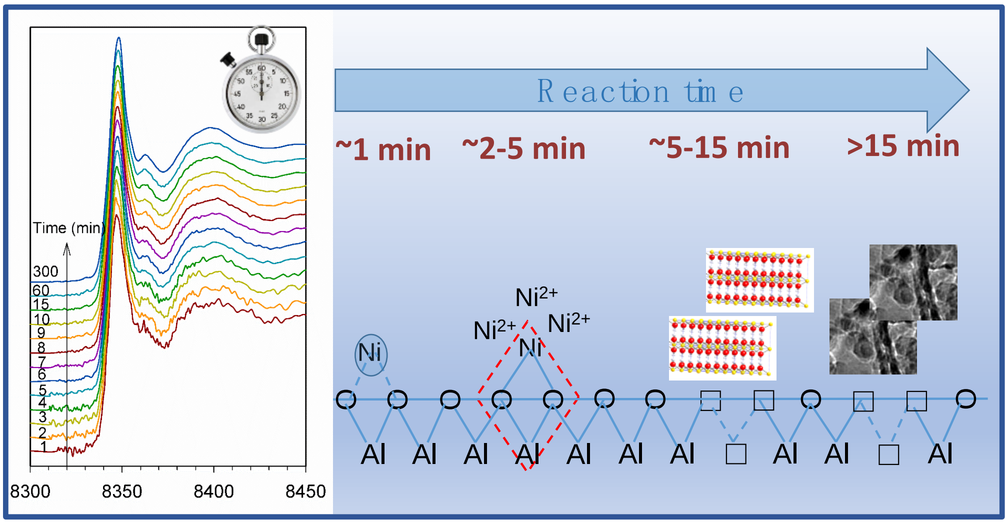
The formation of mixed metal-aluminum surface precipitates, such as layered double hydroxide (LDH) phases, is an important pathway for natural attenuation of toxic transition metals, but the formation process and detailed reaction mechanism at mineral/solution interface are not fully understood owning to the inability of existing kinetic methods (i.e., *ex-situ* batch, stirred-flow systems, and pressure-jump relaxation). In this research, we employed a quick-scanning extended X-ray absorption fine structure spectroscopy (QEXAFS) technique coupled with a flow-through cell to monitor the nickel adsorption/precipitation process on γ-alumina surfaces. Our experiment achieved a time resolution of minute-scale for EXAFS characterization, which in turn demonstrated an increasing second shell for Ni-Ni/Al scattering (3.09Å) with reaction time, with Ni-Ni coordination number (CN) increasing from 1.1 to 3.8. This revealed a rapid transition of inner-sphere surface adsorbed nickel to a mixed metal nickel-aluminum (Ni-Al) LDH precipitate within five minutes, providing strong evidence to conclude that surface precipitation can occur on a rapid time scale similar to as surface complexation in our particular system. Additionally, based on these *in-situ,* real-time QEXAFS data, we exclude pure phase nickel hydroxides as an intermediate phase for LDH formation mechanisms. This information suggested that mixed-metal LDH solids as potential geochemical reaction products should be considered during even short term modeling of nickel speciation in soil, sediments, or mineral systems.



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KN21

Redox properties of biochar and its application in the environmental remediation

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Biochar produced from biomass waste has been extensively used in soil carbon sequestration, soil amendment and pollution restoration. In recent years, studies have reported that after biochar was introduced into soil, there were many interface reactions between biochar and soil pollutants and microorganisms, which were closely related to their redox properties. This presentation will talk about (1) the effect of biomass source and pyrolysis temperature on the electron donating capacity (EDC) and electron accepting capacity (EAC) of biochar; (2) biochar-involved redox reactions for metal immobilization; (3) effects of soil active species such as iron minerals, small organic acids, and microbes on metal immobilization via biochar-involved redox reactions; and (4) Fe-biochar involved redox reactions for soil metal immobilization.

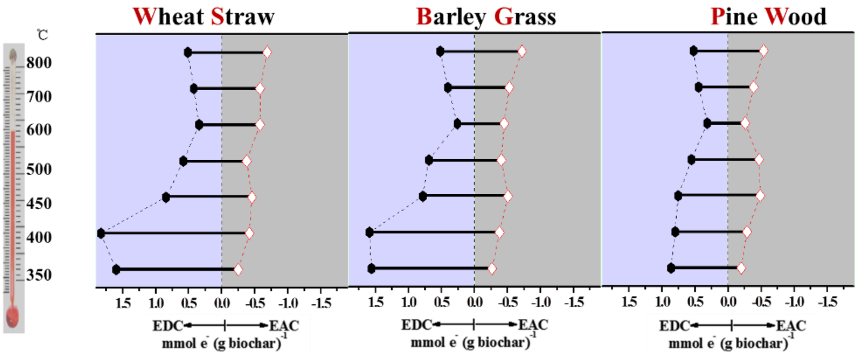

Figure 1: EDC and EAC of biochar at different pyrolysis temperatures

Figure 1 shows that pyrolysis temperature was the dominant factor influencing EDC and EAC of biochar, and Biochar <600°C has higher EDC, while biochar >600°C has high EAC. Biochar produced at low temperatures had a “battery-like” electron transfer mechanism due to its rich redox functional groups. Due to graphite-like structure and edge heteroatom defects, high temperature biochar had “conductive” electron transfer mechanism. Biochar can provide electrons or be as electron shuttle for Cr(VI) reduction immobilization. Fe(III) minerals inhibit biochar for Cr(VI) reduction due to oxidation of –OH group and formation of Fe-C complex. Biochar can mediate small organic acids or microbes to enhance Cr(VI) reduction immobilization. Fe-biochar can immobilize soil As(V) through formation of Fe(III)-As(III)/As(V) precipitates (Figure 2)

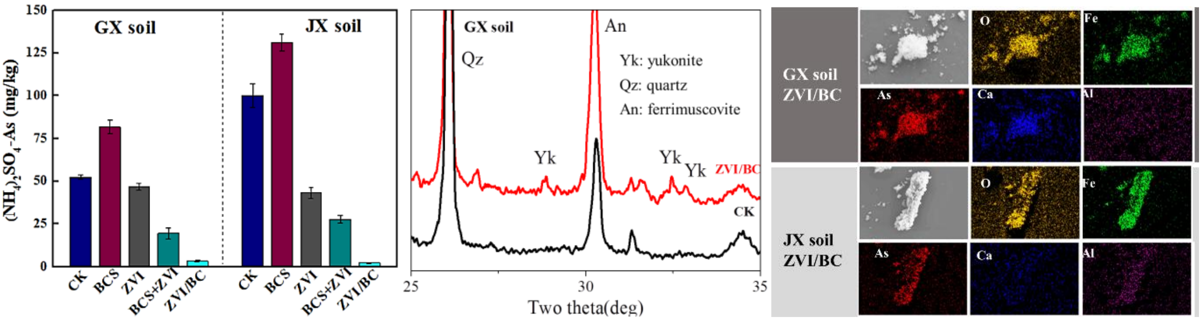

Figure 2: Fe-biochar can immobilize soil As(V) in two soils through formation of Fe(III)-As(III)/As(V) precipitates

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KN22

Intercomparison and refinement of surface complexation models for U(VI) adsorption to goethite based on a metadata analysis

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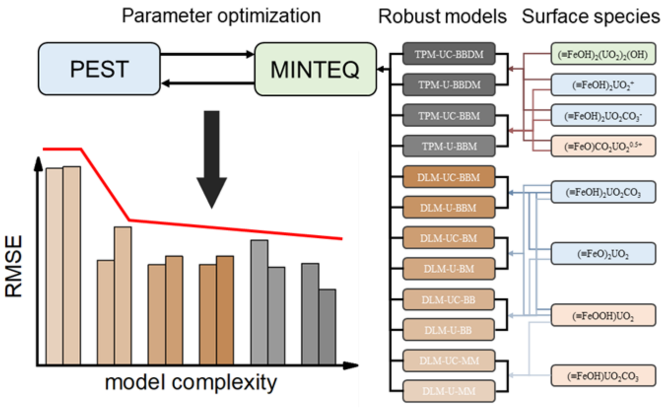
Adsorption of uranium to goethite is an important partitioning process that controls uranium mobility in subsurface environments, for which many different surface complexation models (SCMs) have been developed. While individual models can fit the data for which they are parameterized, many perform poorly when compared with experimental data covering a broader range of conditions. There is an imperative need to quantitatively evaluate the variations of the models and to develop a more robust model that can be used with more confidence across the wide range of conditions. We conducted an inter-comparison and refinement of the SCMs based on a metadata analysis. By seeking the global best fit to a composite dataset with wide ranges of pH, solid/sorbate ratios and carbonate concentrations, we developed a series of models with different levels of complexity following a systematic roadmap. The goethite-uranyl-carbonate ternary surface complexes were required in every model. For the spectroscopically informed models, triple plane model was found to provide the best fit, but the performance of the double layer model with bidentate goethite-uranyl and goethite-uranyl-carbonate complexes was also comparable. Nevertheless, the models that ignore the bidentate feature of uranyl surface complexation consistently performed poorly. The goodness of fitting for the models that ignore adsorption of carbonate and the charge distributions was not significantly compromised compared with their counterparts that considered those. This approach of model development for a large and varied dataset improved our understanding of U(VI)-goethite surface reactions and can lead to a path for generating a single set of reactions and equilibrium constants for including U(VI) adsorption to goethite in reactive transport models.



Surface denticity > Charge distributions > Carbonate adsorption

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Stability of U(VI) on surfaces of montmorillonite and UO_2

PL5

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Adsorption and surface-mediated redox reactions on mineral surfaces can control the mobility of uranium in subsurface environments. Clays such as montmorillonite provide substantial amounts of the reactive surface area in many subsurface environments, and montmorillonite-containing materials are used in the storage of spent nuclear fuel. U(IV) oxide (UO_2) is the dominant constituent of spent nuclear fuel, and it is present in uranium-bearing ores for which mining wastes can pose environmental risks. Reactions on the surface of the clay mineral montmorillonite and UO_2 were explored using a combination of adsorption and isotope tracer studies and X-ray absorption spectroscopy.

A chemically-reduced montmorillonite with Fe(II) in its structure was capable adsorbing and reducing U(VI) to U(IV), which is an overall less mobile oxidation state of uranium. Reduction was more extensive at low ionic strengths, which enabled U(VI) to interact with both edge sites and cation exchange sites of the montmorillonite. Uranium immobilized by reaction with the clay at low ionic strength was more resistant to bicarbonate-induced mobilization than uranium from reactions at higher ionic strengths that prevented uranium from accessing cation exchange sites. We also developed a non-electrostatic surface complexation model to interpret the equilibrium adsorption of U(IV) on reduced montmorillonite as a function of pH and sodium concentration. Using ^{236}U as an isotope tracer, we observed exchange of adsorbed and dissolved U(VI) on unreduced montmorillonite.

A pure UO_2 material was synthesized in the laboratory. Oxidation of its surface occurred in water even in the absence of oxygen. X-ray photoelectron spectroscopy provided evidence for the presence of U(V) and U(VI) species on the U(IV) oxide surface. In experiments with UO_2 and the soluble ^{236}U isotope tracer, no isotope exchange was observed between the aqueous and solid phases even after 47 days of reaction. The lack of isotope exchange indicates that UO_2 is both stable and not undergoing recrystallization in anoxic water over these experimental timescales.

SS1

Enhanced catalytic activity of OMS-2 for carcinogenic benzene elimination by tuning Sr^{2+} contents in the tunnels

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Cryptomelane-type manganese oxides (OMS-2) have been intensively investigated for application in the degradation of organic compounds, and doping metal ions into the OMS-2 nanoparticle are a common way to modifying its performance[1, 2]. In this study, we reported a novel strategy to enhancing catalytic activity of OMS-2 for carcinogenic benzene elimination by tuning Sr^{2+} concentration in the tunnels[3]. An obvious decrease ($\triangle T_{50}$ = 27°C and $\triangle T_{90}$ = 37°C) in degradation temperature T_{50} and T_{90} (corresponding to benzene conversions at 50% and 90%, respectively) was observed. The origin of Sr^{2+} doping positive effect on degradation activity was theoretically and experimentally investigated by CO temperature-programmed reduction, $^{18}O_2$ isotope labeling, and density functional theory calculations. The result confirmed that increasing Sr^{2+} concentration in the OMS-2 nanomaterial not only promoted the lattice oxygen activity, but also facilitated the generation of more oxygen vacancy defects, thus considerably promoting the degradation performance of this nanomaterial.

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Transport of enzymes in quartz sand column partially coated with goethite: effects of pH and humic acid

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Interaction with soil organic matter (SOM) and minerals may affect the mobility and catalytic properties of enzymes in nature. This study gives insight into how the effect of purified Aldrich humic acid (PAHA) on the transport behaviors and enzymatic activity of proteins in goethite coated sand column. Lysozyme (LSZ) and acid phosphatase (ACP) were selected as model proteins and important soil enzymes, respectively. With pH increased from 5 to 8, the mobility of LSZ decreased, while that of ACP increased. LSZ and ACP have observed the highest retention in porous media when they were close to the isoelectric point of the protein. PAHA reduced the zeta potential and enhanced the particle size of LSZ, which significantly reduced the mobility of LSZ. This inhibiting effect was decreased when PAHA/LSZ mass ratio was 0.4 at pH 8. However, PAHA increased the transport of negatively charged ACP at both pH 5 and 8, due to the competition for adsorption sites on porous media and the steric hindrance caused by PAHA adsorption. Since LSZ has high structural stability, its activity in the effluent was still high; while the structural stability of ACP is low, ACP undergoes greater activity changes during the transport process than LSZ. Co-transport of PAHA reduced the perturbation on enzyme activity to a certain extent. This study demonstrated that the charge characters and structural stability of enzymes need to be considered to better predict the overall effect of NOM and mineral on the transport and fate of enzymes.

SS3

Nano-gold decorated TiO$_2$, and ZnO for NO$_x$ degradation: new photocatalytic materials for the improvement of air quality

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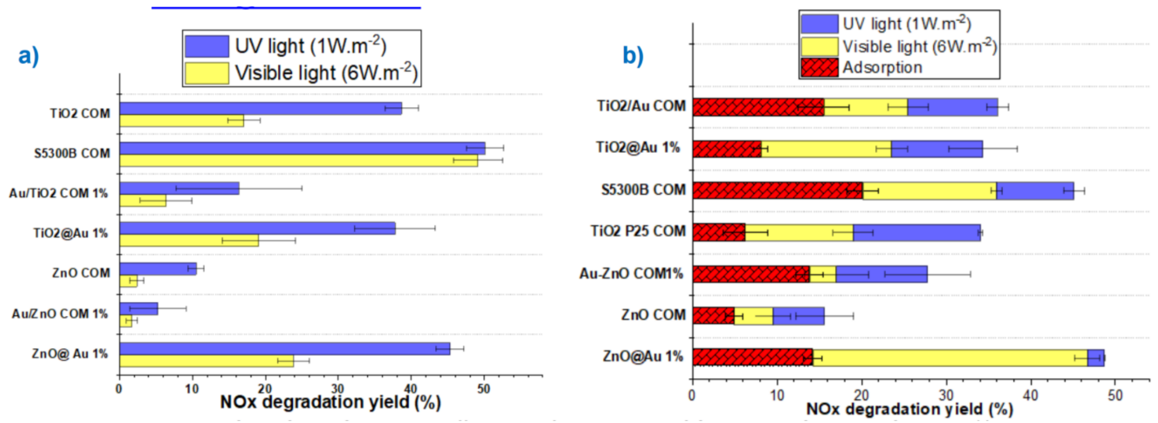

Figure 1: Photocatalytic NOx (NO$_2$ + NO) removal efficiency of commercial (COM) bare TiO2 and ZnO or 1 wt % gold decorated oxides compared to home-made 1 wt % Au decorated TiO$_2$, ZnO under a) 400 ppb NO + 20ppb NO2 and b) 400 ppb NO$_2$ + NO 10ppb**. **The materials were deposited on mortar surfaces (3-4 g.m^{-2}) by spray.

Advanced oxidation processes (AOPs) like photocatalysis are environmentally friendly techniques, acting at standard pressure and temperature conditions for the removal of pollutants in water or in the air. Thanks to this photocatalytic process, functionalized building materials can be achieved: air pollutants removal, self cleaning ability and anti-bacterial properties [1,2] . TiO$_2$ P25 Degussa® (TiO$_2$ COM) has been used as a reference material to improve the air quality thanks to its ability to degrade gaseous toxic pollutants under UV and visible light irradiations [1] . Many efforts have been made to increase its photocatalytic efficiency under visible light. For examples, TiO$_2$ doping, or mixing with other semi-conductors including ZnO & WO$_3$, or surface modification by dye molecules or graphitic carbon nitrides, have been reported [1,2]. One innovative approach is to use the localized surface plasmon resonance effect (LSPR) of metallic nanoparticles (MNPs), such as Au and Ag, deposited on the surface of the metal oxide semi-conductor [3] . This work presents a comparative study on the photocatalytic degradation of NO and NO2 (400ppb) obtained with various metallic oxide semi-conductors: commercial TiO$_2$ (P25 powder and formulated photocatalytic dispersion (S5300B)), ZnO powder and nano-gold decorated commercial TiO$_2$ and ZnO. Homemade Au-decorated oxides were also tested. They were prepared by the photodeposition of a molecular or gold salt precursor on bare TiO$_2$ and ZnO commercial powders. Correlation between the physical-chemical properties of these materials and their photocatalytic response for NOx degradation was studied. Results presented in Figure 1 show that the performances of TiO$_2$ was higher under NO than under NO$_2$. Formulated TiO2 had higher air depollution efficiency compared to the other commercial oxides. Moreover, we observe that Au-ZnO photocatalyst prepared with our procedure (ZnO@Au 1%wt) exhibited a strong NO$_x$ removal efficiency under UV and visible irradiation: the NO abatement was higher than the one obtained with TiO$_2$ P25 and the NO$_2$ abatement was higher than the one obtained with the formulated TiO$_2$. The home-made nano-gold decoration of ZnO increases the NO and NO$_2$ oxidation to NO3- selectivity and offers an interesting alternative to TiO$_2$ material. The nature of Au-ZnO interface and the low surface defects of ZnO seem to be major factors for NOx removal improvement efficiency of the material [3] .

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Reactive transport of rare earth elements: surface complexation with quartz surfaces and modeling investigations

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Rare Earth Elements (REE) are not only considered as high-technology components but also as contaminants of emerging concern creating long-term ecological effects when released into ecosystems. However, there is a lack of comprehensive investigations on their mobility, environmental fate and transport in geochemical settings. In addition, most of the previous studies reported adsorption of one or a few REE onto minerals, and knowledge on dynamic changes of the entire REE patterns in natural porous media is scarce. Here, we have thoroughly examined the interactions of the entire REE group with 100-300 µm quartz sand particles under water-saturated flow conditions. Both batch and dynamic column experiments are conducted at environmentally relevant geochemical conditions.

Adsorption of REE on the quartz surface was investigated over a wide range of pH and varying REE concentrations. As typically encountered for cations, REE binding increased with increasing pH value. Results from batch experiments showed that there is a stronger adsorption for middle REE as compared to light REE or heavy REE. A surface Complexation Model (SCM) based on inner-sphere coordination with silanol groups has been developed for quartz sand, which successfully predicted both sorption edges and sorption isotherms.

We also observed the REE competitive binding in the column experiments where the middle REE are preferentially adsorbed compared to the light and heavy REE. Tracer experiments showed that a homogeneous flow predominates in the sand-packed column. We then developed a transport model using batch-derived surface complexation constants and flow parameters, which account for physical and chemical processes in the column system. This combined model can well describe the breakthrough curves of REE in sand columns under various hydrochemical conditions. These results have strong implications for an accurate assessment of the transport behavior of REEs in natural systems.

Fe-Chitosan complexes for oxidative degradation of emerging contaminants in water: structure, activity, and reaction mechanism

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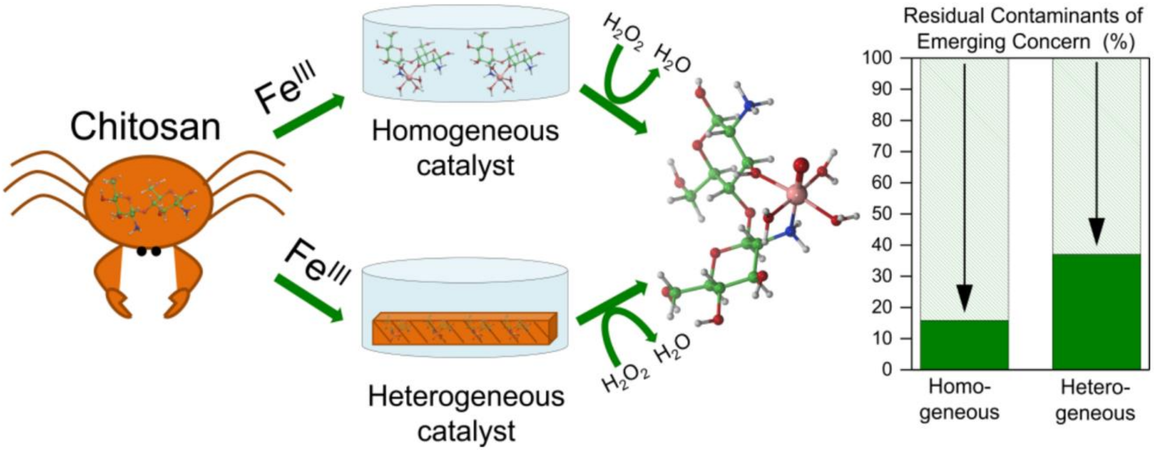

Versatile and ecofriendly methods to perform oxidations at near-neutral pH are of crucial importance for processes aimed at purifying water. In this direction, chitosan (CS) is a promising starting material owing to its accessibility, biocompatibility and ability to form stable films and complexes with metals. CS is a biopolymer derived from the deacetylation of chitin through which a number of acetamide groups have been replaced with amine (-NH2) groups. The raw material for CS production, crustacean exoskeleton, is inexpensive, rendering the large-scale production of CS economically feasible from this renewable resource. Apart from the low toxicity and the other beneficial features of this biopolymer, a distinctive feature of CS from a chemical standpoint is the high density of amine groups at the C-2 positions. This feature enables chitosan to form stable complexes with metals, a property that is exceptional among biopolymers. Here, we report a novel chitosan-based organometallic complex that was tested both as homogeneous and heterogeneous catalyst in the degradation of contaminants of emerging concern in water. The stoichiometry of the complex was experimentally verified with different metals (Cu(II), Fe(III), Fe(II), Co(II), Pd(II), and Mn(II)) and we identified chitosan-Fe(III) complex as the most efficient catalyst. This complex effectively degraded phenol, triclosan, and 3-chlorophenol in the presence of hydrogen peroxide. The molecular structure of the polymer-metal complex was also defined through a combination of experiments and quantum chemical density functional theory calculations. A putative ferryl-mediated reaction mechanism was proposed based on experimental data, density functional theory calculations, and kinetic modeling. Finally, a film of the chitosan-iron(III) complex was synthesized and proven a promising heterogeneous catalyst for water purification.

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SS6

Evaluation of heavy metal availability in soils near former zinc smelters by chemical extractions and geochemical modelling

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Risk assessment of agricultural soils contaminated with heavy metals requires information on their partitioning between the soil solid phase and soil solution and their solution speciation. Multisurface modelling (MSM) is an important tool to predict the partitioning and speciation of heavy metals. However, calcareous clay soils contaminated by smelting and mine waste have received little attention yet in MSM studies. Moreover, these soils feature properties which require specific attention to enable accurate metal speciation modelling and risk assessment. MSM requires important input parameters including the size of the geochemically reactive heavy metal pools and the reactivity of soil organic matter (SOM) for metal binding. In this study, 6 paired soil samples were taken nearby former Zn smelters and at further distance. The geochemical reactivity of heavy metals was determined using soil extraction methods with both 0.43 M HNO_3 and 0.005 M DTPA. For both extraction methods, the reactivity of heavy metals was higher in soil samples taken nearby former Zn smelters than in soil samples from further distance, especially for Cd, Pb, and Zn. Furthermore, the amounts of heavy metals extracted with 0.43 M HNO_3 were consistently larger than those extracted with 0.005 M DTPA, although the results of both extraction methods were strongly correlated. The reactive SOM fraction (HA+FA+HON) in the soil samples varied between 6.2 and 43% with an average of 24%. For dissolved organic matter (DOM), the FA+HON fraction in the 0.01 M $Ca(NO_3)_2$ soil extracts ranged from 30 to 57% with an average of 40%. The accuracy of the MSM predictions of the solubility of Cd in nearly all soil samples was higher when using the results of the 0.005 M DTPA extraction method as model input as compared to the amounts extracted with 0.43 M HNO_3. The same was found for Ni in the calcareous soil samples and Zn in the samples taken near former Zn smelters. Measurement of the geochemical reactivity of heavy metals by the 0.005 M DTPA extraction method and the reactivity of SOM is recommended when using MSM for predicting the partitioning and speciation of heavy metals in smelter slag-contaminated calcareous clay soils.

A novel phosphate-modified calcite adsorbent using for fluoride removal: Synthesis, efficiency, and defluoridation mechanism

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Fluoride pollution in groundwater is a serious problem threatening millions of people all over the world. Calcite is considered as an ideal F adsorbent owning to its low cost. To further enhance its performance, we synthesized P-modified calcite with a series of phosphate concentrations. After modification, BET specific surface ares increased dramatically. FTIR, TEM, and ^{31}P solid-state MAS NMR analysis showed the formation of nano-sized hydroxyapatite (HAP) after modification. As a result, the modified calcite exhibited a up to 10 times higher F removal efficiency than prestine calcite at low F concentrations (i.e., 0.5 mM). However, at high F concentration (e.g., 5 mM), the enhancement is insigificant. This contrary performance was further interpreted by the ^{19}F solid-state MAS NMR analysis, which showed that a surface F-adsorbed calcite species reveaved from the δ_{F-19} = -122ppm dominated at low F concentration whereas CaF_2 precipitates (δ_{F-19} = 108 ppm) formed at high F concentration. Our results demonsrated the immense potential of developing modified calcite as a cost-effective F adsorbent in broad F concentration range and the powerful ability of solid-state MAS NMR spectroscopy in characterizing light-element-bearing amorphous species in researches of environmental science.

SS8

Prediction of nano-magnetite stoichiometry in aqueous solution

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Magnetite (Fe_3O_4) nanoparticles, which are ubiquitous in subsurface environments and highly sensitive to various environmental conditions, are of great scientific interest due to their magnetic, magneto-optic, semiconductor, and redox properties. In particular, magnetite nanoparticles are widely used for environmental remediation. Magnetite contains one Fe(II) and two Fe(III) in its structure (R = Fe(II)/Fe(III) = 0.5) and all its interesting properties are due to the presence of Fe(II). However, Fe(II) can be easily oxidized to Fe(III), which leads to the formation of maghemite (γ-Fe_2O_3) (R = 0). This transformation is complex because magnetite and maghemite form a solid-solution, that is, a continuum of intermediate compounds so-called non-stoichiometric magnetite can form with $0 \leq R \leq 0.5$. Although many studies focused on the impact of magnetite stoichiometry (R) on its reactivity, no quantitative model can predict the effect of environmental factors such as pH and E_h on magnetite stoichiometry, yet.

Experimental solubility studies of stoichiometric magnetite nanoparticles (≈10 nm) were conducted over a large pH range (3-11) in 10 mM NaCl solutions under anaerobic conditions. The impact of E_h was investigated by exposing stoichiometric magnetite to known amounts of H_2O_2 in order to obtain a set of magnetites with different initial stoichiometries (R_{ini} = 0.1, 0.2, 0.3, 0.4 and 0.5). The effective stoichiometry R_{eff} of the nanoparticles at equilibrium was determined indirectly by measuring $[Fe(II)]_{aq}$ after filtration and directly by measuring [Fe(II)] after acid digestion of the solid and X-ray Magnetic Circular Dichroism (XMCD) spectroscopy at the SOLEIL synchrotron.

The results show that the concentration of dissolved Fe(II) increases with decreasing pH and increasing R_{ini}. Hence, pH exerts a strong control on R because of the H^+-promoted dissolution of Fe^{2+}. In particular, stoichiometric magnetite nanoparticles cannot exist at moderately acidic pH (< 7) despite a high magnetite concentration (2.5 g/L) or the addition of an excess amount of 2500 µM dissolved Fe(II). In other words, at pH < 7, even though anaerobic conditions are preserved, nano-magnetite successively transforms to quasi-maghemite with dissolved Fe^{2+}. This observation renders numerous mechanistic interpretations of magnetite physico-chemical behavior in many studies where magnetite stoichiometry was not monitored, questionable.

Finally, all data are used to develop a predictive thermodynamic solid-solution model for the effect of pH and redox conditions on magnetite stoichiometry. This model may be a powerful tool for both, tuning magnetite properties for practical applications as well as the prediction of magnetite behavior in complex aqueous systems (natural waters, biological fluids, etc).

Coupled effects of Mn(II), pH and anionic ligands on the reactivity of nanostructured birnessite

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While the oxidative capacity of nanostructured birnessite-type manganese oxide has been widely investigated, no comprehensive work exists on the combined effects of dissolved Mn(II), pH and inorganic anions on sorption and redox reactions of organic contaminants with MnO$_2$. Herein, we have showed how molecular interactions with MnO$_2$ surfaces controlled on the removal kinetic behavior, which depended on contaminant type and co-existing anions. Competition between contaminant and Mn(II) for binding at the edge sites determined the initial kinetic step, while buildup of Mn(II) at both edge and vacancy sites continuously decreased adsorption and subsequent oxidation over time. Redox interactions of Mn(II) to MnO$_2$ surfaces was a pH dependent process, and high pH favored Mn(II) removal and comproportionation reaction, thus decreasing adsorption and oxidation processes.[1,2] ATR-FTIR and XRD data showed that only high Mn(II)/MnO2 ratio (2.3) and high pH ($\geqslant$ 8) enabled surface-catalyzed oxidation of Mn(II) by molecular oxygen and then formation of manganite (γ-MnIIIOOH). However at lower Mn(II)/MnO$_2$ ratio, MnO$_2$, positively charged from the adsorption of Mn(II) ions, adsorbed more effectively anions such as phosphate or silicate and thus reducing interactions with organic compounds. These results highlight the combined suppressive effects of Mn(II), pH and naturally occurring anions on the reactivity of nanostructured birnessite, and have strong implications on the fate of organic contaminants in terrestrial and aquatic environments.

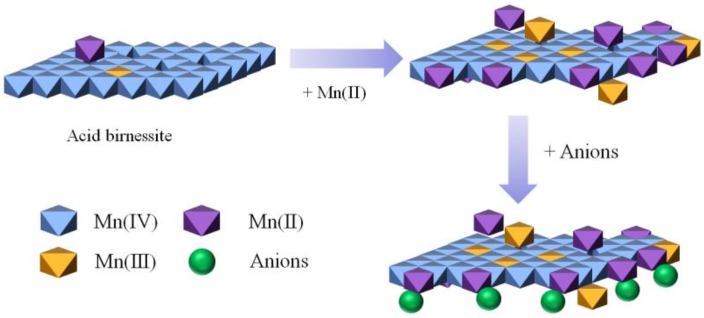

Figure 1: A proposed mechanism for the combined suppressive effects of dissolved Mn(II), pH and naturally occurring anions on the reactivity of nanostructured birnessite.

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SS10

The influence of the gel or resin layer thicknesses on the measurement of metal accumulation in DGT.

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DGT (Diffusive Gradients in Thin films) is a technique based on the accumulation of a target analyte after diffusion through a diffusive gel [1]. For metals, the accumulation in the resin results from the contribution of all the metal species, with metal complexes contributing according to their lability degree (ξ). The lability degree of a system can be measured as the ratio of the actual complex contribution to the metal accumulation over the maximum contribution that would be achieved if dissociation was fast enough to instantaneously reach equilibrium with the free metal at all the relevant spatial domain. Each metal species contribution depends on the configuration of the DGT device (characterized by the thickness of the resin and of the diffusive gels used). An independent and complementary information on the dynamic characteristics of the sample can be obtained from accumulation measurements with different DGT configurations.

The accumulation of Ni in solutions containing different nitrilotriacetic acid (NTA) concentrations has been measured with several DGT devices containing combinations of resin(s) and diffusive gel(s) resulting in total different thicknesses. ξ increases as either the thickness of the diffusive gel (δ^g) or of the resin (δ^r) increase [2]. These results are reproduced with a simulation tool that considers the diffusion reactions in the DGT device by solely fitting the kinetic dissociation constant of the NiNTA complex. Diffusion coefficients have been measured in a diffusion cell and speciation has been obtained with the software VMINTEQ. The decrease of the lability degree as the total NTA concentration increases has been explained from the formation of $Ni(NTA)_2$. Simple analytical expressions have been reported for the dependence of ξ on δ^g or δ^r.

In conclusion, the thickness of the resin and/or diffusive gels of a DGT device can be optimized to improve the correlation with bioavailability. Likewise, using a set of DGT configurations to measure the contribution of complexes in natural waters, a set of equations can be written to recover dynamic characteristics of individual complexes or some fractions with similar chemical properties determined by chemical speciation (e.g. inorganic and organic pools) [3].

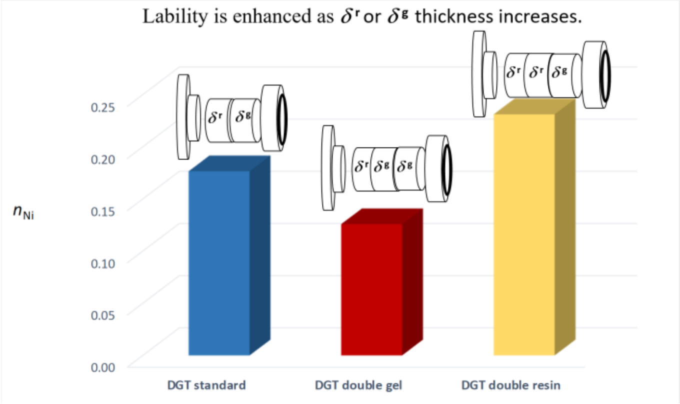

Figure 1: Different configurations of DGT devices with different thicknesses δ^g or δ^r accumulate different number of Ni moles.

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Heterogeneous degradation of refractory pollutants by peroxymonosulfate activated by cobalt-doped FeS

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A series of cobalt-doped FeS (x%Co-FeS) nanoparticles prepared using a hydrothermal method were introduced as catalyst to generate powerful radicals from peroxymonosulfate (PMS) for endocrine disrupter bisphenol S (BPS) degradation in waste water. The kinetic results showed that cobalt-doped FeS exhibited better catalytic performance than FeS in PMS oxidation for BPS degradation, and the activation efficiency increased with the increase of the proportion of Co. The pH was controlled with 50mM phosphate buffer, more than 95% of BPS (20 mg/L) was removed within 20 min at the pH = 6 by 7% Cobalt-doped FeS. And the excellent activation effect could be obtained at a broad range of pH 4-11. The degradation efficiency increased with the increase of catalyst load and PMS concentration, and the presence of different background ions and different temperatures had little impact on the degradation, implying suitable for all kinds of sewage environment. In order to explore the reaction mechanism, ethyl alcohol, isopropyl alcohol, benzoquinone and Sodium azide were used as the quenching agents, showing the co-existence of a variety of reactive oxygen species (ROSs) in the reaction system, such as $SO_4^{\bullet-}$, $O_2^{\bullet-}$ and $^1O_2$. Moreover, the catalysts presented favorable recycling and stability in the repeated batch experiment, which provides the implication on the application of cobalt-doped FeS as a promising heterogeneous catalyst in the degradation of organic contaminants in Fenton like systems.

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SS12

Evaluation of dyes sorption onto hierarchical Faujasite based on multiscale approaches

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Dyes are considered as big and complex groups of toxic organic substances which become a major environmental concern. These are primarily discharged from industries like food, textile processing, pulp, paper, leather and printing industries. Different types of dyes for instance acidic, basic, reactive and dispersive dyes are used widely. The decontamination processes are often based on the use of adsorbents with specific properties such as high adsorption efficiency, which is the case of nanostructured materials such as porous silicas, clays or zeolites, … Thanks to the modulation of the synthesis conditions, it is possible to finely adjust the properties of the adsorbent, such as the structure, the porosity, the surface charge, and thus to carefully control and tune the driving forces of the sorption. Our objective was to focus on the impact of porosity on the mechanisms of interactions, with materials having high sorption capacity and different degree of porosity (micro, meso, macro). Well known faujasite type zeolite (FAU) has been selected for its high Cation Exchange Capacity (CEC), and the possibility to obtain hierarchical faujasite to workaround the problems of diffusion limitation. Modified faujasite was synthesized by using a base to generate leaching in addition to a surfactant as a structuring agent, thus leading to hierarchical materials. Several characterization methods have been carried out such as N_2-Sorption-Isotherm, ^{29}Si-NMR, Infrared and X-ray diffraction to evaluate structural and textural properties.

Several dyes (sDiA and Basic Fuchsin) were chosen for their properties of size, charge, functional group, and their sorption effiency were determined. The adsorption isothems were studied at natural pH and using depletion method. The adsorption capacity varies with the properties of dye and the materials. The displacement enthalpy associated with the adsorption of the dye molecules was estimated using isothermal titration calorimetry. This approach offers the possibility to evaluate the effect of porosity, but also of the surface chemistry (hydrophilicity) using direct measurements as function of the loading. In addition, Second Harmonic Scattering (SHS) has been used as a local technique to evaluate the interaction at the FAU/dyes interface. Isotherms and polarization resolved SHS measurements seem to demonstrate that linear dyes interact strongly with the particles by entering to the pores whereas bulky dyes and anionic ones adsorb only on the external surface. To the best of our knowledge, this is the first time that such macroscopic and local approaches are combined to evidence the effect of confinement on the sorption.

Adsorption capacity of the corrosion products of nanoscale zerovalent iron for emerging contaminants

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Despite the extensive use of nanoscale zerovalent iron (NZVI) in water and soil remediation, no data exist on the reactivity of secondary iron minerals formed upon the NZVI corrosion[1,2]. Herein, we investigated the oxidation kinetics of NZVI by monitoring the variations of pH, oxidation–reduction potential (ORP) and dissolved Fe(II) concentration, and then examined the reactivity of resulting oxidized particles for the adsorption of an emerging contaminant (nalidixic acid (NA)). NA adsorption was found the greatest on oxidized particles and negligible on the fresh NZVI. Interestingly, the formed secondary mineral phases exhibited an unusual pH adsorption curve with an unexpected great adsorption at alkaline pH values. X-ray photoelectron spectroscopy and high resolution-transmission electron microscopy revealed a gradual increase in the Fe(II) content at the surface of the magnetite phase over the reaction time. Additional experiments and surface complexation modeling showed that the enhanced adsorption of NA onto the secondary magnetite is due to the formation of surface bound Fe(II). Fe(II) is released into the solution because, for instance, of the presence of organic buffer molecules, decreased surface Fe(II) and NA adsorption at alkaline pH values. This work sheds light on an overseen aspect of the reactivity of secondary iron minerals resulting from NZVI passivation, which can bind co-existing emerging contaminants and then affect their fate in the environment.

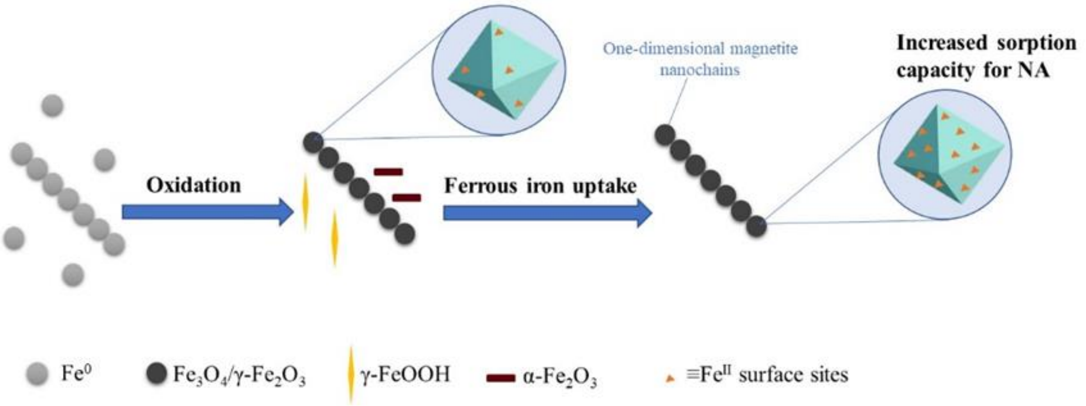

Figure 1: Formation of surface bound Fe(II) on the NZVI secondary minerals would enhance NA binding and affect its mobility in the environment

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Selective sorption of phytate and orthophosphate on ferrihydrite with different aggregation

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The aggregation states of ferrihydrite play an important role in controlling its reactivity. In this study, sorption of phytate (IHP) and phosphate (Pi) on two aggregation states ferrihydrite (loose aggregate in fresh ferrihydrite, FHFO; dense aggregate, HFO) was investigated by batch experiments combined with synchrotron-based X-ray diffraction (XRD) and P K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Both IHP and Pi have a higher sorption capacity on FHFO than on HFO, especially for IHP. And the ratio of maximum adsorption amount of Pi to IHP-Pi (calculated as Pi) is 0.6 for FHFO, while that is 3.27 for HFO. In the presence of both IHP and Pi, FHFO preferentially sorbs IHP because the higher sorption affinity constant of IHP than Pi on FHFO, while HFO preferentially sorbs Pi because IHP with a larger molecule size than Pi might hardly diffuse into the micropore structure of HFO. Both IHP and Pi form surface precipitates on FHFO with similar proportion of precipitate in P at pH 6. Compared to FHFO at the same condition, Pi and IHP sorb and precipitate less on HFO, with IHP more significant. These findings have useful implications on the fate of organic phosphorus and inorganic phosphorus in the environmental.

Microstructure of Al-substituted goethite and its adsorption performance for Pb(II) and As(V)

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Naturally occurring goethite commonly undergoes Al-substitution, while how changes in microstructure induced by Al-substitution affect the interactive reaction of Pb(II) or As(V) at the goethite-water interface remains poorly understood. This study reveals the structural properties of Al-substituted goethite and its adsorption behavior for Pb(II) and As(V) by multiple characterization techniques and Charge Distribution-Multisite Surface Complexation (CD-MUSIC) modeling. Al-substitution caused an obvious decrease in the length-to-width ratio in goethite particles and a slight decrease in the proportion of (110) facets. The presence of Al-O sites and higher surface roughness induced by Al-substitution contributed to a higher inner Stern layer capacitance (C_1) and surface charge density of goethite. CD-MUSIC modeling results further revealed that the affinity constant of Pb(II) complex (log K_{Pb}) at the goethite-water interface and the adsorption capacity of goethite for Pb(II) decreased with increasing amount of Al-substitution, while an opposite tendency was observed for As(V) adsorption. The dominant species of both Pb(II) and As(V) on goethite were bidentate complexes, and Al-substitution had a minor impact on the abundance of Pb(II) and As(V) complexes on the surface of goethite. Overall, these experimental and modeling results provide new and important insights into the interfacial reactivity of Al-substituted goethite and facilitate the prediction of the environmental fate of heavy metals.

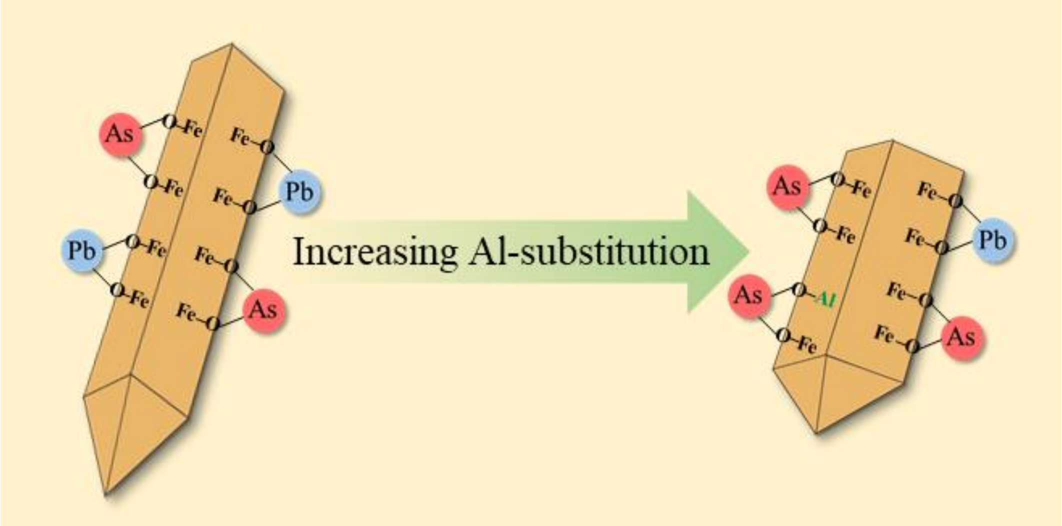

Figure1: Al-substitution decreased the adsorption capacity of goethite for Pb(II), while increased that for As(V).

Acknowledgements

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SS16

Inter-laboratory validation of vapor pressure measurements of two endocrine-disrupting molecules: 4-tert-octylphenol & 4-n-octylphenol using gas saturation and static method

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Octylphenols are harmful endocrine disrupting chemicals available in food contact materials [1]. They are transfered into foodstuff via the migration process. To evaluate the health risk assessment of the consumer, this process has become a main interest to many food institutions and laboratories. It is affected by different factors including contact duration and temperature, nature of foodstuff as well as the physicochemical properties of the chemical migrant [2]. Accordingly, we were interested in determining experimentally several physicochemical properties of these migrants (aqueous solubility, octanol/water partition coefficient, vapor pressures). In this study we will present vapor pressures of the two isomers: 4-tert-octylphenol and 4-n-octylphenol (MW= 206.32 g.mol^{-1}) due to the lack of experimental data in the literature.

The vapor pressures of the two aforementioned alkylphenols were determined using two different methods in two different laboratories. In USEK (Lebanon), we adopted the dynamic gaz saturation method that allows measurements ranging between 10^{-5} and 10^{3} Pa [3]. In UCBL1 (France) a static apparatus was used. The latter allows direct measurements of the vapor pressures between 1 Pa and 200 kPa [4].

The vapor pressures of n-octylphenol were determined by the dynamic method in the range between 3 10^{-3} and 670 Pa. No comparison data could be found in the literature. Therefore we compared the interlaboratory measurements (dynamic and static methods). The agreement is good as the relative deviation is between 2 and 15%.

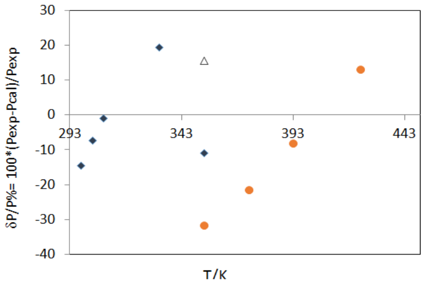

Fig.1: Comparison of vapor pressures from dynamic. Method with: ♦, Ref [5], ○, static apparatus.

In Fig.1 we reported the relative deviation between the vapor pressures obtained by the dynamic method (3 10^{-2} and 1450 Pa, particularly wide pressure range) and those obtained by the static apparatus or by literature.A quite good agreement is observed with Verevkin [5] data (1 to 15%) and with those obtained by the static apparatus except for the points at limit of measurement of the static apparatus (below 10 Pa,) where the deviation reaches 30%.

In the future, we plan to measure more physicochemical properties to cross-reference with vapor pressures in order to evaluate the dangerous risk of migration of food contact chemicals on human health.

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SS17

Photosensitized degradation of paracetamol by rose bengal-modified clays and alginate materials/rose-bengal

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The presence of contaminants in natural waters (ground and surface waters) and their accumulation in plants and animals is a worldwide major concern. Among the large variety of substances that human activity introduces into the environment are organic pollutants. Within this group, pharmaceuticals are the ones that have given rise to most concern and studies in recent years. Just in the EU, the use of some pharmaceutical products, such as paracetamol, is estimated to be similar to the pesticides amount. Paracetamol is a widespread painkiller and antipyretic drug which is widely consumed throughout the world. Nowadays, it is one of the most frequently found drugs in hospital effluents, water treatment plants, rivers and sludge. Therefore, removing and/or degrading this contaminant in aqueous media is of great interest since clean water is essential for life. In this context, photosensitized degradation is an environmentally friendly option for organic pollutant removal. These processes are mostly based on the use of a photosensitizer that absorbs ultraviolet or visible radiation and reacts with water-dissolved molecular oxygen generating reactive oxygen species (ROS). Subsequently, ROS are responsible for degrading organic compounds dissolved in water. Rose bengal (RB) is a non-toxic dye that can be used as photosensitizer. It is known that RB dissolved in water photogenerates singlet oxygen (O2(1Δg)), a type of ROS [1]. Probably, the main challenge of photosensitized degradation processes is to remove the photosensitizer from water at the end of the photo oxidative cycle. This inconvenience can be solved by incorporating this substance in an easy-to-handle green support without losing its photochemical properties and allowing easy separation. This work aims to synthesize materials composed by RB, montmorillonite clay (MMT) modified with aminopropyltriethoxysilane (APTES) and alginate biopolymer for the formation of MMT-APTES-RB beads in order to generate O2(1Δg) and then photodegrade paracetamol in water.
The ability of the synthesized beads to photogenerate ROS was studied by oxygen uptake experiments. For this purpose, ground-state oxygen consumption (O2(3Σg-)) was determined using a specific electrode and a furfuryl alcohol solution (1×10-4M) as substrate for O2(3Σg-) variation recording. After determining that the beads are capable of photochemically generating O2(1Δg), photodegradation assays of paracetamol were performed. These experiments were carried out with irradiation at a wavelength between 500 and 550 nm (green LED) in the presence and absence of MMT-APTES-RB beads under constant stirring. In addition, the adsorption of the contaminant on the beads was studied in the dark. The assays were performed with a paracetamol solution (1×10-4M) at a pH above its pKa so that the phenolic group is deprotonated and reactive towards O2(1Δg). UV-Vis spectra of paracetamol were recorded every 10 min for 90 min. The spectra
of the studies in the presence of beads in the dark and those of direct photolysis (irradiation in the absence of beads) showed no variation over time. On the other hand, spectra collected during experiment of irradiation in presence of beads showed spectral changes (decrease in absorbance and appearance of new bands) indicating that paracetamol is degrading and new species are being formed. Results in the present study demonstrate that the synthesized material can photogenerate O2(1Δg) in aqueous solution and this ROS is capable to photodegrade paracetamol dissolved in water. In addition, no quantifiable adsorption of the pharmaceutical was observed on the bead. Photodegradation of this contaminant by direct irradiation was not observed.
In addition to the ability to generate O2(1Δg) and degrade organic contaminants dissolved in water, these materials are economical and environmentally friendly because their components are non-toxic and because their synthesis does not involve toxic solvents and does not generates waste. Finally, it is also important to point out that these beads are easy to handle, so they can be effortless removed from aqueous media. These features enable MMT-APTES-RB beads to be proposed as water decontamination materials from emerging contaminants such as paracetamol.

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Water dispersible colloids and related nutrient availability in Amazonian Terra Preta soils[1]

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Amazonian Dark Earths (or terra preta de índico) are known as highly fertile soils that can maintain elevated crop yields for centuries. While this fertility was frequently ascribed to the presence of black carbon, the availability and colloidal binding of major nutrients received limited attention. We examined the size distribution and the elemental compositions of water-dispersible colloids (WDC) in both forested and cultivated Terra Preta topsoils (0-10 cm, Anthrosols), as well as in their adjacent non-Terra Preta controls (Acrisols) via asymmetric flow field-flow fractionation (FFF). Liquid-state ^{31}P-nuclear magnetic resonance (NMR) spectra, black carbon content, and scanning electron microscope (SEM) images were also obtained. We found that WDC in Terra Preta soils contained a significant proportion of organo-mineral associations in the size range 30-300 nm, whereas, in contrast, water-dispersible nanoparticles with a diameter <30nm were dominant in the adjacent Acrisols. The shifts to larger WDC sizes in the Terra Preta soils went along with elevated pH values, as well as with elevated contents of Si, Al, Fe, Ca and organic matter-containing particles. Also P concentrations were enriched in both the water-extractable phase (WEP) and WDC extracts of Terra Preta soils relative to the adjacent Acrisols. The higher pH values and Ca ion concentrations promoted the involvement of soil organic matter (SOM) into the formation of larger-sized colloids consisting of kaolinite-like clay minerals, iron oxides and Ca ions in the Terra Preta soils. The elevated content of Ca in Terra Preta soil colloids may also contribute to the retention of P, likely via bridging of anionic P like orthophosphate to SOM. Preventing soil acidification is thus not only to be recommended for Acrisols, but also for maintaining colloidal structures and related fertility in Terra Preta soils.

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Molecular understanding of humic acid-promoted hydrolysis of phytate through stabilizing a conserved catalytic domain in phytase

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As a potential phosphorus (P) pool, organic phosphorus (P_o) is of fundamental importance for sustainable P utilization. The enzymatic hydrolysis of P_o, particularly phytate due to its multiple phosphate groups, enhances bioavailability of P in the presence of dissolved organic matter (DOM) in natural soils. However, the in situ kinetics of hydrolysis to release inorganic phosphate (P_i) reacting with soil metal cations and molecular mechanisms of catalytic performance of phytase associated with DOM in environmentally relevant conditions remain unclear. Here, using liquid-cell atomic force microscopy (AFM), we present a model system to quantify the in situ heterogeneous nucleation dynamics of phytase-released P_i from phytate precipitated by Ca^{2+} and Fe^{3+} ions on bare and organically-coated (-OH and -COOH) micas in the presence of humic acid (HA). We observe that higher concentrations of HA result in faster nucleation rates of calcium/iron phosphate (Ca/Fe(III)-P) on (un)modified mica substrates. A combination of AFM-based PeakForce quantitative nanomechanical mapping and quantitative Raman band-narrowing and spectrum fitting of phytase and its mutant and conserved active catalytic domains (ACD, SRHGVRAPHD) reveals the dynamics of HA-promoted hydrolytic activity of phytate through a noncovalent HA-phytase complexation to enhance the formation of a more ordered, stereochemically-favored catalytic domain following stabilization of an unordered non-catalytic domain by HA wrapping phytase [1]. Moreover, based on the single-molecule force spectroscopy (SMFS) measurements, we further detect the enhanced formation of H-bonding between amides in ACD interacting with HA in the absence of phytate (Figure 1). Following the addition of phytate, the calculated contour length (L_c) and the free energies (ΔG_b) of functional groups within ACD binding to mica/HA demonstrate the formation of the ordered intermediate structural states of ACD following its covalent binding to phytate. These determinations provide the molecular-scale evidence regarding the detailed mechanisms of HA-stabilization of the organization of secondary structures of ACD in phytase through chemical functionalities in ACD noncovalently interacting with HA [2]. We suggest that similar studies of the interactions of other soil enzymes/proteins and nutrients/pollutants may reveal predominant roles of dissolved organic matter in controlling elemental cycling and fate on environmentally relevant mineral interfaces.

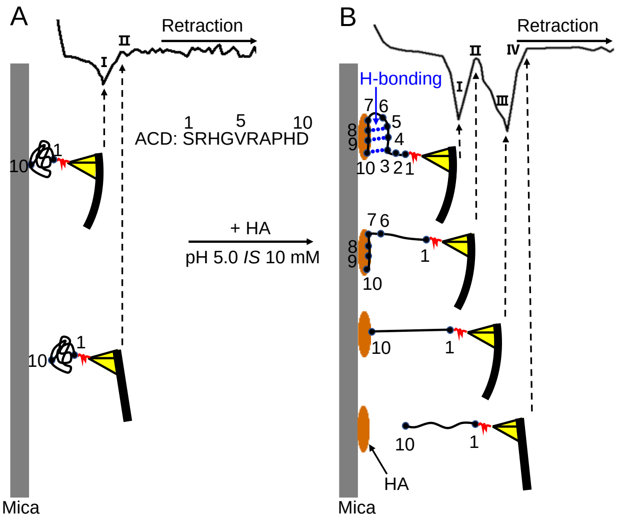

Figure 1: ***The acquired F-D curves and corresponding rupture force patterns of ACD detached from the mica/HA interface. (A) ACD-functionalized tip is approached toward, retracted (I) and separated II) from the mica. A single force-peak curve suggests that ACD is not fully extended and maintains its secondary structure as evidenced by measured L_c. (B) Following the adsorption of HA on mica, the F-D curves obtained from ACD detached from mica with adsorbed HA exhibit double-force peaks, followed by retraction (I-III) and separation (IV) of ACD. At position I, as the***

ACD-functionalized tip is retracted, the ACD sequence unfolds through the concurrent and/or sequential rupture of H-bonding (shown by blue dots); this is enhanced by the HA-ACD interaction formed between amide bonds. Once H-bonding is broken, the extended ACD is further stretched until reaching a holding force, resulting in fully unfolding of ACD. (II) The holding force is abruptly decreased due to an increment of L_c of the extended ACD. (III) Continued retraction of the ACD-functionalized tip through stretching unfolded ACD leads to the detachment of amino acids 7-9 in ACD from HA until the last holding force is reached. (IV) Complete separation of amino acid 10 of ACD from HA reduces the holding force because of an increment of L_c of fully unfolding of ACD.

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SS20

A new protocol for executing acid/base titration on organic matter applied to seven new IHSS batches

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In soil contamination studies, Natural Organic Matter (NOM) holds a crucial role because of its size, ubiquity,and high reactivity. NOM's reactivity towards various contaminants is related to the charge of acid-basegroups: carboxylics and phenolics. Various quantification methods have been applied to their study, acid/base potentiometric titration being the most reliable one. However, the experimental methodology and interpretation of data is still a debate.

The current acid/base titration protocol for organic matter performs consecutive titrations in the same sample at least at three different ionic strengths. The salt used to change ionic strength is added at low pH. This process takes several days. It brings a significant risk of pH electrode drift and greatly dilutes the sample. The salt addition at low pH is not optimal for curve positioning due to the very low charge.

Also, there is neither an explicit description in how to position the different ionic strengths protonation curves (meaning that they are implicitly positioned during the titration) nor how to determine the absolute charge at the initial titration pH (Q0), in the literature.

We bring forth a faster titration method by reducing the number of titrations; improve curve positioning by modifying the ionic strength at high pH where the measured charge is high and submit a Q0 determination by extrapolation of the curves to an asymptotic value (Fig1).

Titrations where conducted with seven different IHSS new batches and produced good quality raw data. The results where modelled using a double-Langmuir-Freundlich equation to explain the chemical binding and a recent permeable sphere Poisson-Boltzman model (SPBT)1 to describe the electrostatic contribution.

Experimental data fitting was executed using a home-made Fortran program coupled with PEST as described in Pinheiro et al 1. The obtained results describe very well the experimental curves.

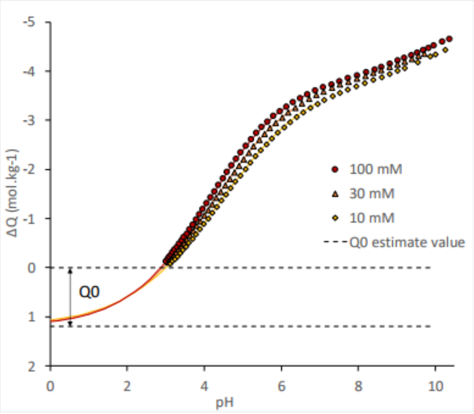

Figure 1: Proton titration curves for Standard Suwannee River Fulvic Acid (3S101F) with different Ionic strengths (electrolyte concentrations: 10, 30 and 100 mM)

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Nanoscale imaging of simultaneous occlusion of nanoplastics and glyphosate within soil minerals

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Nanoplastics are widely distributed in soils and could interact with other exposed organic contaminants such as pesticides, leading to enhanced toxicity to plants and soil beneficial microorganisms. These combined organic pollutants can also interact physiochemically with mineral matrices to be selectively preserved and occluded. Inclusion organics within growing minerals and pore spaces of mineral aggregates are potentially inaccessible to plant root cells and soil microorganisms, but the microscopic mechanisms that control occlusion processes remain poorly understood. Here we use time-resolved atomic force microscopy (AFM) to observe how soil minerals interact in situ with different functional groups of polystyrene (PSFG) mixed with glyphosate (PMG). Our results show that the PSFG-PMG complexes are occluded within calcite and iron hydroxide particles through growing hillocks and aggregation, respectively. The free energies of binding between functional groups of polystyrene and calcite surfaces measured by AFM-based dynamic force spectroscopy in the presence of different concentrations of PMG account for molecular interactions involved in the occlusion process and the effect of PMG concentrations. These in situ nanoscale observations and molecular-scale energetic measurements may provide insights into the immobilization of both nanoplastics and pesticides by soil minerals, with potential implications in multiple pollutant sequestration.

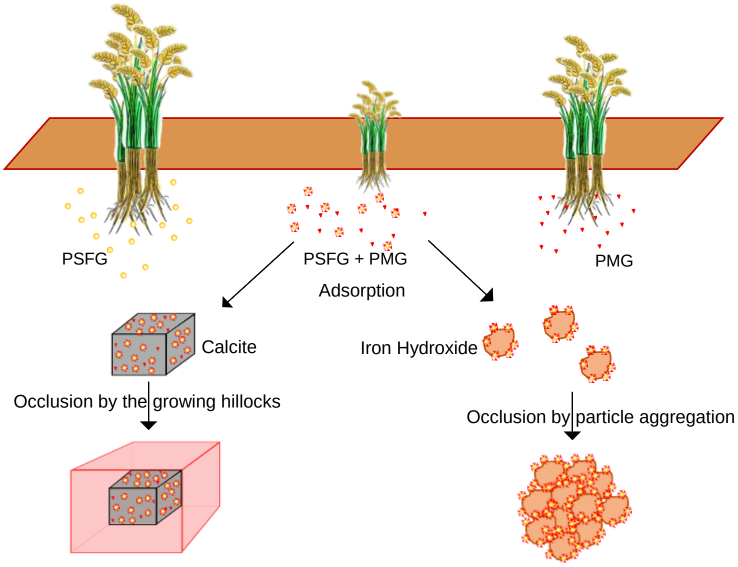

Figure 1: Schematic of the adsorption and occlusion of PSFG and PMG by calcite or iron hydroxides and toxicity of PSFG and PMG taken up by rice plants. The occlusion of PSFG or PSFG + PMG within calcite crystals and iron hydroxides through the growing hillocks and aggregated particles, respectively. Mixed PSFG and PMG would inhibit the cell/whole plant viability and growth prior to the occlusion, and the stronger inhibition effect occurred in the mixed PSFG and PMG, compared to PSFG or PMG alone.

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SS22

As(III) adsorption-oxidation behavior and mechanisms on Cr(VI)-incorporated schwertmannite

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Schwertmannite, chromate (Cr(VI)), and arsenite (As(III)) usually coexist in acid mine drainage (AMD) and surrounding areas, but their interactions and mechanisms are poorly understood. We have determined the behavior and mechanisms of As(III) adsorption–oxidation on Cr(VI)-incorporated schwertmannite (Cr-Sch), with co-adsorption and redox of As(III) and Cr(VI) on pure schwertmannite as a comparison, using batch experiments combined with in situ quick X-ray absorption spectroscopy (Q-XAS). As(III) adsorption isotherms on Cr-Sch can be better described by the Freundlich equation, ascribed to the presence of multiple heterogeneity adsorption sites. With increasing Cr(VI) incorporation, both As(III) adsorption and oxidation increase remarkably. Additionally, with increasing pH from 3 to 7, As(III) adsorption increases, whereas its oxidation increases up to pH 5 and then decreases at higher pH due to the surface passivation by the generated Cr(III) precipitates. Cr(VI) speciation (aqueous vs. structural) seems to have no significant effects on As(III) adsorption–oxidation if structural Cr(VI) is available. The As(III) adsorption–oxidation pathways and mechanisms on Cr-Sch include, firstly, adsorption of As(III) through surface complexation and anionic exchange, followed by a direct redox between As(III) and Cr(VI) on the surface; the newly generated As(V) and Cr(III) then co-adsorb or precipitate on the mineral surface, simultaneously decreasing their toxicity and mobility. These new insights are essential to predict the mobility and availability of As and Cr in schwertmannite-rich natural environments.

Molecular sorption mechanisms of Cr(III) to organo-ferrihydrite coprecipitates using synchrotron-based EXAFS and STXM techniques

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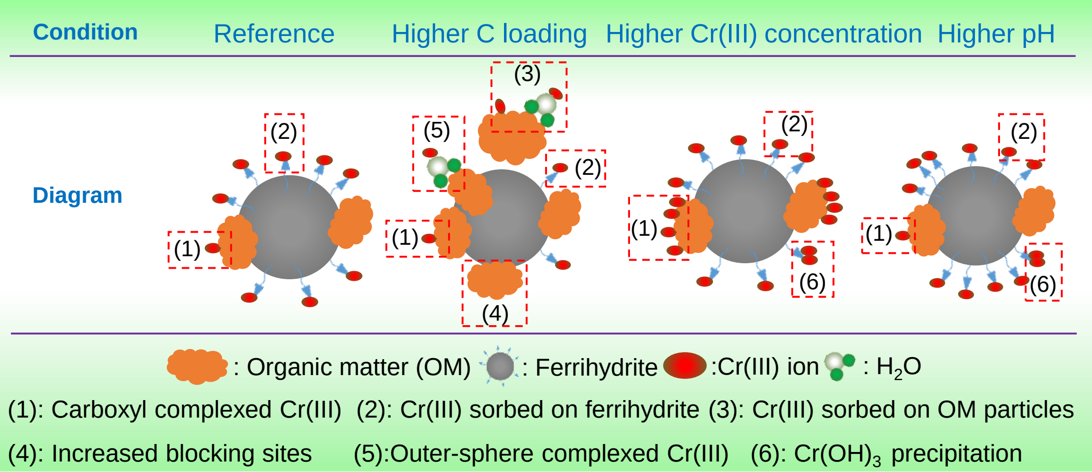

Figure1: Schematic description of the sorption mechanisms of Cr(III) to OFC under different conditions.

Ubiquitous organo-ferrihydrite coprecipitates (OFC) significantly affect the mobility and availability of Cr in soil through sorption, but the underlying sorption mechanisms remain unclear at the molecular level. Due to the potential formation of OFC in agricultural soils with returned crop straws, we synthesized OFC with rice/rape straw-derived carbon (C) sources and different loadings. The molecular sorption mechanisms of Cr(III) to the synthesized OFC under different conditions were investigated by Cr K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy and scanning transmission X-ray microscopy (STXM). Cr(III) sorption by OFC decreased with increasing C loading and decreasing pH, regardless of C sources. Moreover, inhibition of Cr(III) sorption to OFC with high C loading occurred when ionic strength (IS) increased, suggesting the presence of outer-sphere complexed Cr(III). EXAFS analysis revealed that more Cr(III) were bound to ferrihydrite of the OFC at a relatively high pH, and organically bound Cr(III) enhanced when increasing C loading and decreasing IS. STXM analysis strongly suggested that C loading reduced Cr(III) sorption through blocking the binding sites on the ferrihydrite, which overwhelmed Cr(III) retention by the direct binding of Cr(III) to carboxyl of the particulate organic matter (OM) and OM coated on the ferrihydrite fractions of the OFC. These findings facilitated the comprehensive understanding of the sorption mechanisms of Cr(III) to OFC at the molecular level, which will assist the prediction of Cr(III) mobility in soils, particularly for Cr(III)-contaminated agricultural soils with the application of crop straws.

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SS24

Molecular mechanisms of cadmium sorption to rape straw biochars using ^{13}C nuclear magnetic resonance spectroscopy and Cd L_3-edge X-ray absorption near-edge structure

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In this study, two biochars were prepared throught the pyrolyzation of rape straw at 400 ℃ (RB400) and 700 ℃ (RB700) for investigating Cd sorpiton at different pHs. The biochars and their Cd sorption products were characterized using a series of techniques including ^{13}C nuclear magnetic resonance spectroscopy (^{13}C-NMR) and Cd L_3-edge X-ray absorption near-edge structure (XANES). Cd sorption capacity of biochars increased with increasing pH from 7.0 to 8.0, regaredless of RB700 or RB400. However, at the same pH, RB700 exhibited a higher efficiency in Cd sorption than RB400, which might be caused by more abundant pore structure and micropores in RB700. ^{13}C-NMR indicated carboxy and alkyl carbon functional groups were probably involved in Cd immobilization by biochars. Moreover, Cd L_3-edge XANES analysis demonstrated the complexation of Cd by organic ligands were mainly responsible for Cd immobilization by RB400. But the predominant species of Cd on RB700 was $CdCO_3$ (73.9%), implying surface precipitation was the main mechanism for Cd sorption to RB700. These findings promote the understanding of Cd sorption mechanims by rape straw biochars, which have a potential application on the remediation of Cd contaminated water or soil, especailly at alkaline condition.

Building an effective concentration signature for Zn availability from 4 techniques to a stream

P1

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Nutrient or toxicant availability to biota in aquatic systems is mediated by its supply from the water towards the active surface, where uptake occurs. If the internalization process for a metallic element is the limiting step, the key species is the free metal ion concentration, as postulated by the Free Ion Activity Model. If the limiting step is the supply across the medium, the thickness of the diffusion layer (or Diffusive Boundary Layer, δ^{DBL}) becomes also a very relevant parameter, as this thickness modulates the capability of the metal complexes to dissociate before reaching the active surface (1). So, the effective concentration available for a given organism depends on its δ^{DBL}. When the characteristic length of an analytical technique matches this δ^{DBL}, it will provide a good estimate of the effective concentration of this nutrient or pollutant for this organism. Gathering effective concentrations from various techniques, one can build up a signature (or spectrum) characterizing this aqueous medium.
This new concept has been applied to the availability of Zn in the water of a small tributary (Osor stream) of the river Ter (Girona, Spain). Besides routine techniques (such as ICP-MS or ion chromatography), four speciation techniques have been used (2). Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) (3) and PIM (Polymer Inclusion Membrane) (4) have provided [Zn^{2+}]. Diffusion Gradient in Thin films (DGT) (5, 6) devices with different configurations (i.e. different number of resin discs or gel discs) have provided labile concentrations corresponding to different characteristic lengths. Anodic Stripping Voltammetry with Linear stripping scan (LASV) has provided the labile concentration in a much shorter timescale (2). From the various effective concentrations, the signature was assembled and lability degrees for each of the characteristic lengths were determined.

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P2

Physical and chemical fractionation of soil organic carbon in relation to long-term phosphate fertilization

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Studies of the effect of long-term phosphorous (P) fertilization on the evolution of pools of soil organic carbon (SOC) is of great relevance for climate change, soil fertility, and soil degradation. In the present study, archived top soils of a long-term field experiment (46 years) with a different P fertilization (0, 90, 180, 240 kg P_2O_5 ha^{-1}), sampled in 15, 24, 46 years after the start of the experiment were studied to elucidate relations between changes in P-status and different fractions of SOC. A physical and a chemical method were used to fractionate SOC and the results were compared. In the physical method, mass density fractionation, after a robust ultrasonic dispersion, was used to differentiate a light (OC_{light}) and heavy (>1.8 g cm^{-3}) (MOC_{phys}) SOC fraction. By chemical oxidation with NaOCl, followed with mineral dissolution with HF, three SOC fractions were distinguished, i.e. labile (OC_{labile}), mineral-associated (MOC_{chem}), and recalcitrant or residual (ROC) OC. The light fraction OC_{light} (80%±1%) overlaps with the labile fraction OC_{labile} (68%±2%) and recalcitrant fraction ROC (17±2%), and the variation in PO_4 surface loading (0.5-2 µmol m^{-2}) has no significant influence on these fractions. The heavy fraction MOC_{phys} is 19±3% of total SOC, which is comparable to the amount of mineral-associated fraction determined after chemical oxidation MOC_{chem} (15±1%). The heavy fraction MOC_{phys} slightly decreased with the increase of the PO_4 loading, however mineral-associated fraction MOC_{chem} increased with the increase of PO_4 loading. Interpretation with a core-shell model revealed that both MOC_{phys} and MOC_{chem} can be accommodated in the compact part of the electrical double layer (L = 0.7±0.1 nm) around the surface of oxide particles. The decrease of the heavy fraction MOC_{phys} with PO_4 loading is quantitatively in agreement with the increase of space occupied by the adsorbed PO_4 ions. The increase of mineral-associated fraction MOC_{chem} with PO_4 loading is possibly due to a lower negative particle charge, leading to exclusion of OCl^- anions from the compact part of the interface in the chemical oxidation, resulting in a reduced oxidation of MOC by NaOCl. Therefore, the observed PO_4 loading dependency of MOC_{chem} can be an artifact of the experimental methodology. The physical method may be a more reliable approach to determine mineral associated soil organic carbon, which shows a slight decrease after long-term P fertilization.

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P3

Photocatalytic activation of sulfite by maghemite (γ-Fe_2O_3) towards iohexol degradation with magnetic separation

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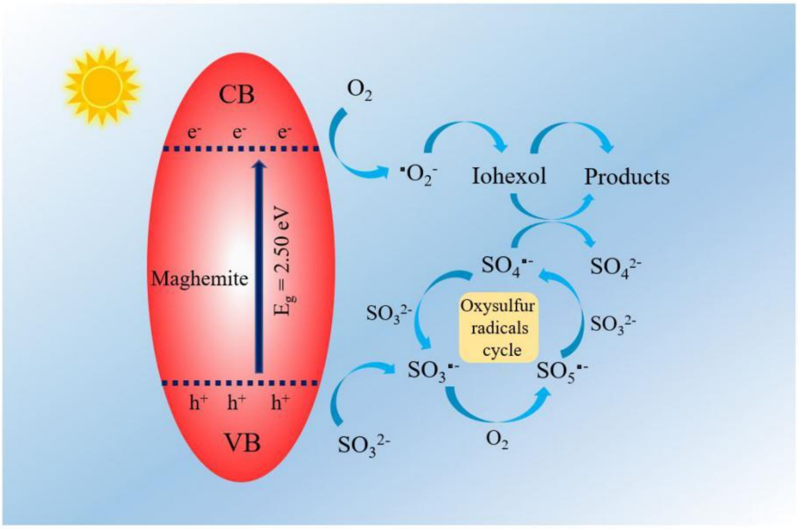
Photocatalytic activating sulfite (S(IV)) system has been gradually regarded as a promising advaned oxidation technology for recalcitrant contaminants treatment over the past decade. Herein, a magnetic mineral existed in nature, maghemite (γ-Fe_2O_3), was been used as an activator for sulfite activation towards the degradation of iohexol under visible light irradiation. With the addition of 0.5 mM S(IV), the degradation efficiency of iohexol reached up to 91.3% at 15 min under neutral condition whereas it could be negligible without S(IV). And the effects of experimental parameters, including catalyst dosage, S(IV) amount, initial pH, dissolved oxygen and co-existing substrates were systematically investigated. The maghemite/S(IV)/vis system exhibited a great performance for iohexol oxidation via a wide range of pH (3-10) and neutral condition was the optimal. Quenching experiments and electron spin resonance (ESR) analysis revealed that photoinduced holes and dissolved oxygen played crucial roles in the generation of $SO_3^{\bullet-}$ and its subsequent transformation to oxysulfur radicals, respectively. And the dominant reactive species for iohexol degradation were $SO_4^{\bullet-}$. Compared with other common agents, such as hydrogen peroxide, persulfate and peroxymonosulfate, maghemite/S(IV)/vis system possessed the strongest capability for contaminant degradation. Furthermore, the reactivity of maghemite was not been impaired even after 10 runs and its dipersion and separation in solution was convenient due to mild magnetism. Our results demonstrated that maghemite could be a potential photocatalyst for sulfite activation in wastewater treatment.



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P4

Passivation of heavy metals in landfill soils of mountain villages by phosphorus-containing substances

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The garbage produced by villages and towns often contains a large number of harmful substances including heavy metals, especially As，Cd and Pb，which bring various environmental problems to the countryside[1]. Since phosphorus-containing passivating agents are affordable and easily available, phosphate rock (PR) and monopotassium phosphate (MPP) were selected as passivating agents for cultivation. This study took the soil (collected from 3 points at 30 meters of the slope from the fan-shaped waste landfill of Yunxi town (105°21′54.78″E, 31°15′27.55″N)) in Yanting County, Sichuan Province of China as the research object.

Compared with GB 15618-2018 of China, Cd in all samples exceeded the standard by 0.8 to 2.1 times, while other heavy metals did not. After BCR sequential extraction (the classification was F1~F4, which represent acid soluble fraction, reducible fraction, oxidation fraction and residual fraction respectively), F1 accounted for 10%-20% of As and Cd, and Pb was dominated by F2, accounting for more than 63%. For further passivation of these 3 heavy metals, PR (0.2%, 0.4%, or 1%) or MPP (0.5%, 1%, or 2%) was added to soils, keeping the field moisture capacity at 60% and temperature at 25 ℃，and then extracted with DTPA after cultivation for 30~60 days. The passivation rate calculation was based on the content before (C1) and after (C2) the cultivation: R=(C1-C2)/C1[2].

On the 30th day of cultivation, PR had activation effect on As, while passivation rate of Cd was 24.5%, and it had no or slightly passivation effect on Pb； MPP had an activation effect on these 3 heavy metals. After 60 days of cultivation, only 0.2% PR had passivation effect on As, the maximum passivation rate was 87.2%. 0.2% and 0.4% PR could passivate 43.6% and 38.5% of Cd, and the passivation rate of PR to Pb was 26.2%-44.8%. The activation effect of MPP to As was lower than that on 30th day. The passivation rate of MPP to Cd was 50.1%~74.3%, and the average passivation rate to Pb was 36.1%.

The results of BCR sequential extraction showed that after 60 days of cultivation, PR and MPP converted As and Pb of F1~F3 to F4, resulting in F4 increased 3.70(As) and 5.75(Pb) times consequently; F1~F3 of Cd were decreased by PR, while F2 of Cd was not significantly changed by MPP, leading to an average increase in the proportion of Cd in F4 by 20%.

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P5

Effects of organic matter–goethite interactions on reactive transport of nalidixic acid: Column study and modeling

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The fractionation of natural organic matter (NOM) and its impact on the binding of quinolones to mineral surfaces and transport behavior under flow-through conditions have been scarcely investigated. In this study, the sorption and transport of a widely used quinolone antibiotic, Nalidixic acid (NA), were investigated in goethite- coated sand (GCS) columns over a wide concentration range (5–50 mg/L) of Leonardite humic acid (LHA), a representative NOM. Simultaneous injection of NA and LHA in GCS columns mutually alter transport of each other, i.e. NA mobility and LHA molecular fractionation. Preloading of GCS column with LHA dramatically facilitated the transport behavior of NA, where nonspecific interactions with LHA-covered goethite surfaces controlled NA mobility. Simulations using a two-site nonequilibrium model showed that a modified sorption rate constant was required to accurately describe the breakthrough curves of NA under these conditions. This altered rate constant suggests that nonspecific interactions of NA on bound LHA may take place as an additional binding mechanism affecting adsorption kinetics. NOM fractionation alters sorption mechanisms and kinetics of quinolone antibiotics, which in turn affect their fractionation. These results may have important implications for an accurate assessment of the fate of these types of antibiotics in aquatic environments.

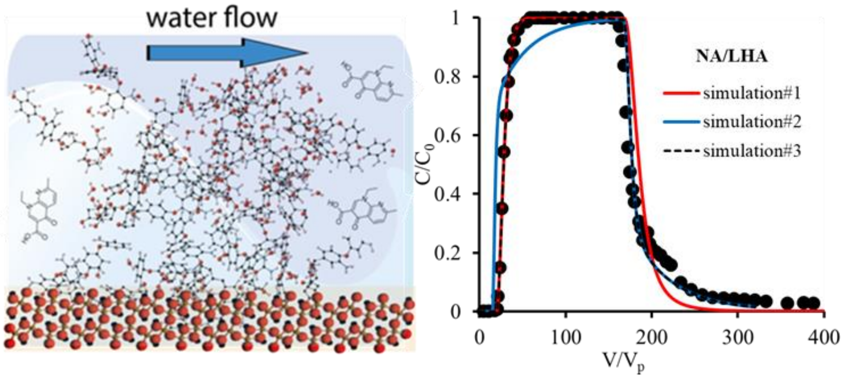

Figure 2: Adsorption of NA and LHA onto goethite under flow-through conditions. Lines are modeling results. 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH in 5 was injected for adsorption and 0.01 M NaCl at pH in 5 was injected for desorption at 0.5 mL/ min.

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P6

Coagulation and sedimentation of imogolite: effect of pH and salt concentration

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Imogolite is a naturally-occurring aluminosilicate mineral, which is commonly found as aggregates like translucent gel films in pumice layers of a volcanic ash soil[1]. Because imogolite is one of main components of clay fraction along with allophane, its chemical structure and physicochemical properties have been examined. Imogolite can be also chemically synthesized[2] and functionally modified. Thanks to its nano-tubular structure and dispersed state in aqueous solution, imogolite attracts attention in recent years as a promising candidate for nano material science[3]. Charging property that determines the colloidal stability of imogolite has been elucidated since its discovery. Imogolite is a hollow fibrous substance with an inner diameter of 1 nm, an outer diameter of 2 nm and a length of several hundred nm. The outer surface is positively charged by protonation of hydroxyl groups of alumina sheet, and the inner surface is negatively charged by deprotonation of silanol groups. Because dissociation behavior of both charge groups depends on solution pH, the amounts of positive and negative charges concurrently sift with a pH change. It is commonly found that the amount of positive charge monotonously decreases with increasing pH that ranges from 3 to at least 10 while the amount of negative charge is zero below around pH 5–6 and appears above the pH and increase with increasing pH. On the other hand, the value of electrophoretic mobility (EPM) of imogolite showed almost positive constant value irrespective of pH change that ranges from 3 to 7–11. Colloidal stability of imogolite has been investigated by soil scientists for half a century and recent material scientists. Karube et al. (1998) found a natural imogolite disperses below pH of 6.5 and aggregates on the alkaline side. Recently, Paineau et al. (2019) reported a phase diagram study of colloidal stability of imogolite in terms of its volume fraction and solution pH. However, at this moment, it is still unclear that the reason why imogolite can aggregate even though its electrophoretic mobility is significantly higher. In this present study, we conducted coagulation experiment in the wide range of pH and salt concentration along with sedimentation experiment and EPM measurement. Coagulation experiment of 50 mg/L of imogolite with different pH and NaCl concentration showed the critical coagulation pH (CCpH) decreased with an increase of NaCl concentration. The CCpH seems to correspond to the pH that the inner surface begins to dissociate. In the range of pH that coagulation occurred, sedimentation experiment demonstrated that temporal variation on interface height of imogolite suspension at 100 mM were faster than others with lower NaCl concentration (1, 10 mM), and the height at 60 min were lower. That is, the flocs formed at 1 and 10 mM NaCl were more bulky than that at 100 mM NaCl. Combined with the knowledge of charging behavior and the result of our coagulation and sedimentation experiments, imogolite tubes may coagulate at 100 mM in contact with tube-side by tube-side because of a supresion of electrostatic repulsion. On the other hand, at lower NaCl concentration, imogolite tubes may attach each other in contact with tube-end by tube-side because of coulombic force.

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Influence of titanium dioxide nanoparticles on metallic trace elements behaviour in soils

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Titanium dioxide nanoparticles (n-TiO_2) are one of the most extensively engineered anomaterials (ENMs) produced worldwide in large quantities due to their innovative properties for various applications in many fields[1]. Their tremendous various applications has led to their wide spread distribution in the environment including urban and industrial waste waters, which are treated in wastewater treatment plants (WWTPs). Sewage sludges coming from these WWTPs are often used as amendment onto agricultural soils, thus unintentionally leading to an accumulation of ENMs including n-TiO_2 into soils.

The objective of this study is to get a better insight into the influence of the presence of n-TiO_2 (rutile, 60 nm) on metallic trace elements (MTE; Cu and Pb) retention onto soils and transfer to the aquifers and surface waters, for a better prediction of their mobility and fate in agricultural soils receiving sewage sludges. To overcome the soil complexity and understand the involved processes, this study is carried out on simplified systems, meaning soil individual phases such as iron oxyhydroxide (goethite), organic matter (humin), and clay (montmorillonite). Adsorption experiments of the selected MTE were conducted on these solid phases by investigating the effect of several parameters (pH, ionic strength, n-TiO_2 and MTE concentrations). Then, the experimental data will be modellized using an integrated multi surfaces approach enabling to describe and predict the behaviour of MTE in soils taking into account the n-TiO_2 presence.

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P8

Ultrasound-synthesized zero-valent iron nanoparticles for Cr(VI) removal, application for the treatment of metal surface processing wastewater

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Zero-Valent Iron (ZVI) is the most commonly used zero-valent metal for environmental remediation [1]. Since the early 1990s, this reducing agent has been used to remediate a wide variety of organic and inorganic contaminants present in various environmental media (ground and surface waters, soils).
Reductive zero-valent iron nanoparticles were prepared for the treatment of Cr(VI) solutions. The ferric ions reduction by $NaBH_4$ was carried out through mechanical stirring or ultrasound irradiation either in an ultrasonic bath or in a 20 kHz cup-horn reactor. The prepared materials have been characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, and N_2 adsorption-desorption at 77 K. The removal of Cr(VI) ions (initial Cr(VI) concentration of 10 mg.L^{-1} or 20 mg.L^{-1}) by the prepared nanoparticles (dose:100 mg.L^{-1} or 10 mg.L^{-1}), was studied as a function of pH (2-8) and contact time (0.5-60 min) in UHQ (Ultra High Quality) water. Cr(VI) removal experiments were also carried out on wastewater from surface treatment industry containing Cr(VI) ions (Cr(VI) concentration of 11.8 mg.L^{-1} or 0.14 mg.L^{-1}) and other metallic ions (mainly Ni(II) at 69 mg.L^{-1}). The metals removal efficiencies were studied for the three prepared ZVI nanoparticles types and compared to the ones in the UHQ water solutions.
The microscopic observations showed iron nanoparticles with diameter in the range 40 nm-80 nm, arranged in chain aggregates regardless the variation of the preparation method [2]. The ultrasonic synthesis allowed to obtain higher BET specific surface area (99 m^2.g^{-1}) for nanoparticles prepared in ultrasonic bath (referred to Fe^0-UB) and for the ones prepared by probe sonication (145 m^2.g^{-1}, referred to Fe^0-CHR) than the ones of sample synthesized in silent conditions (22 m^2.g^{-1}).
The Cr(VI) ions removal in UHQ water solution was found significant at acidic pH. The removal kinetic rates modeled by pseudo first order, are linearly proportional to the BET surface areas of the ZVI nanoparticles. The Cr(VI) removal kinetics are rapid (< 30 min to attain equilibrium) and decrease as increasing the Cr(VI) concentration and as decreasing the iron nanoparticles dose. They are well fitted either by the pseudo first order model or the shrinking particle type model limited by a surface reaction when excess of ZVI nanoparticles is used with respect to Cr(VI). Cr(VI) ions were removed by reduction and co-precipitation of Cr(III) in the form of chromite at pH>7. The more effective and faster Cr(VI) reduction in synthetic solutions by using the Fe^0-CHR ZVI nanoparticles rather than others is explained by their high porosity and specific surface area developed through the 20 kHz ultrasonic synthesis achieved in a cup horn reactor.
These ultrasonically prepared ZVI nanoparticles have proven to be very efficient for the Cr(VI) ions reduction either in UHQ water synthetic solutions or in effluent from metal surface processing industry, and even in the presence of other metal ions such as Ni^{2+} [2]. The ZVI nanoparticles prepared by a 20 kHz ultrasonic probe have been found more effective in removing Cr(VI) ions than any kind of ZVI nanoparticles conventionally prepared. The control of the ZVI nanoparticles dose allows to decrease the Cr(VI) concentration in order to treat industrial effluents at the required environmental standards.

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Wood wastes: from an environmental burden to efficient biochars for pharmaceutical molecules removal in aqueous solution

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Significant amounts of the produced chemicals are rejected in waste water which is routed *via* reglementary circuits to WasteWater Treatment Plants (WWTPs). However WWTPs usualy fail to remove these pollutants due to the used treatment methods incompatibility with the molecules physico-chemical properties. According to recent studies, adsorption onto biochars could be a very interesting method for the organic pollutants removal, especially if applied as a WWTPs tertiary treatment after physical and biological processes. In this work, biochars are tested as organic micropollutants adsorbents in aqueous solutions.

Spruce (Picea abies L.) and pine (Pinus Sylvestris) wood wastes were used as feedstocks for the biochars production. Four kinds of biochars have been prepared from sieved biomass (2–6 mm) issued from the wood Chips (Ch), Barks (Ba), Branches (Br), and Pelletized Chips (PCh). The feedstocks have been pyrolysed at around 600°C and then thermally activated at 900 °C in a PYREKA unit (Pyreg GmbH, Dörth, Germany) under steam (injection of 2.3 mL H_2O/min at room temperature, 10 min residence time). The produced activated biochars have been characterized by using physical N_2 and CO_2 adsorption/desorption at 77 K and 273 K, respectively with ASAP 2020 automative sorptometer to determine their specific surface areas and porous size distributions (Table 1).

Biochar precursor type	SSA (m^2/g) (BET/N_2)	Total mesoporous volume (cm^3/g)	Total microporous volume (cm^3/g)	Total ultra-microporous volume (cm^3/g)
Wood chips (Ch)	***903***	***0.46***	***0.35***	***0.15***
Wood barks (Ba)	***716***	***0.48***	***0.22***	***0.14***
Wood branches (Br)	***730***	***0.48***	***0.28***	***0.10***
Pelletized Chips (PCh)	***616***	***0.17***	***0.30***	***0.14***

Table 1: Physical gas adsorption/desorption results of spruce and pine derived activated-biochars.

The removal kinetics (0-240 min) of three pharmaceuticals at C_0~1 mg/L. namely Carbamazepine (CZP), Diclofenac sodium (DCF), and Ibuprofen (IBF) were investigated on Ch biochar (10 mg) in 1L spring water at pH=7.3. The concentration of the pollutants were followed using an LC-MS/MS apparatus (Perkin Elmer).

Varying removal efficiency (Y%) are found such asY_{DCF} = 96%; Y_{CZP} = 69%, Y_{IBF} = 53%. The adsorption kinetic data of these three molecules onto Ch were well fitted by the second-order model and the equilibrium state was reached after 240 min contact time suggesting a possible chemisorption-driven process [1].

Further investigations are currently undertaken to entirely determine the biochars physico-chemical properties as well as the adsorption kinetics and isotherms for the removal of CZP, DCF and IBF and others micropollutants such as Metoprolol, Benzotriazole, Ofloxacin, Diuron, Acesulfame, Cetirizine, Clarithromycin and Diatrizoic acid, etc.

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P10

Development of new materials for the adsorption of arsenic (V)

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The Chaco-Pampean plain is a large area in Argentina, whose groundwater has high As concentrations exceeding the WHO guideline values for drinking water.[1] This is an important problem especially in locations where people depend on groundwater for drinking. The development of new materials for environmental remediation is a topic of high priority due to the increasing contamination of water. Arsenic is highly carcinogenic after long-term or high-dose exposure thus remediation techniques are continuously investigated to remove it from aqueous media. Although several methods are used to removing As from water, the adsorption method is considered to be one of the most promising technologies due to its low cost, high uptake capacity, great selectivity, and easy equipment handling. Layer Double Hydroxides (LDHs) are promising materials because they have a very high sorption capacity. LDH, also known as hydrotalcite-like-compounds or anionic clays, have been widely used as adsorbents. The general formula of LDHs is $[M^{2+}_{1-x} M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}.yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A^{n-} is an anion incorporated in the interlayer space along with water molecules for charge neutrality. The structure of LDH presents partial isomorphic substitution of Mg^{2+} by trivalent cations. This replacement leads to an excess of positive charge and to a high anion exchange capacity. They are promising materials for the removal of ecologically undesirable anions.

The main objective of this work was to evaluate the ability to adsorb arsenic (V) (arsenate and its protonated species) of an iron-rich LDL (Fe-LDH). This solid was selected because it is not harmful for the environment. Fe-LDH was prepared by the coprecipitation method at constant pH. The solid was characterized by XRD, FTIR, SEM, TEM, DSC, electrophoretic mobility, stability and elemental analysis. To investigate the adsorption kinetics of arsenate, the batch technique for adsorption was used.[2] The effects of various experimental conditions such as contact time, pH, temperature, stirring rate and arsenate concentration were investigated.

The characterization of the sample revealed that Fe-HDL had a high crystallinity and a laminar structure, which was formed by particles of size 30-50nm. Fe-HDL had positive zeta potentials throughout the studied pH range (3-10). Dissolution kinetic studies performed in the pH 3-8 range revealed that the sample is relatively stable at pH greater than 5. It was observed that the arsenate adsorption as a function of time consists of two well-differentiated stages: a rapid one that is completed before 5 minutes of reaction, and a slow one that reaches an apparent equilibrium of the system between 4 and 8 hours of reaction. The amount of arsenate adsorbed over time increased as the initial concentration of the anion increased. The increase in pH produced a decrease in the amount of arsenate adsorbed at any reaction time, probably as a consequence of the decrease in the positive charge of LDH, which translates into a lower electrostatic attraction between the surface and the anions. The increase in temperature and the variation of the stirring rate did not produce significant changes in the adsorption of arsenate. It was also observed that the adsorption of arsenate on Fe-LDH caused charge reversal, as detected by zeta potential masurements, probably due to the formation of inner-sphere complexes between the anions and the surface of the solid. The results of this study show that Fe-HDL is a very effective arsenate adsorbent, and could be used in environmental remediation. Translated into percentages of adsorption, as an example, for a system containing $1x10^{-4}$ M of As and 2 g/L of Fe-LDH content, the studied LDH could adsorb more than 93% of the arsenic.

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Synthesis of montmorillonite-alginate beads applied to the kinetic study of paraquat adsorption

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Paraquat (1′-dimethyl-4,4′-bipyridinium dichloride, PQ) is a quaternary ammonium herbicide. Although its use is restricted within the European Union, as it is considered a highly hazardous pesticide (HHP), it is still used worldwide, so further research into this pollutant is needed. Water pollutants removal is mainly carried out by adsorption processes. These processes require the use of adsorbents with some features such as low cost, accessibility and non-toxicity. Alginate (Alg) - Montmorillonite (Mt) beads have been effective for the adsorption of PQ [1].

The aim of this work is synthesise and characterise alginate beads loaded with a 70 % of montmorillonite (Alg-Mt70) at different resident times in $CaCl_2$ in order to analyse the effect of the ionic gelation process on the PQ adsorption process. In addition, the adsorption kinetic of the pollutant paraquat on Alg-Mt70 beads was evaluated. Beads were synthesised by dissolving sodium alginate in 0.1 M NaCl to form a 1.0 % by weight alginate solution. A set amount of montmorillonite clay was added to this solution and the mixture was homogenised on a mechanical stirrer overnight. This homogenised solution was added dropwise to a 0.1 M $CaCl_2$ solution with a peristaltic pump to produce calcium alginate-montmorillonite (Alg-Mt) beads. The residence times studied of the beads formed in this $CaCl_2$ solution were 30; 60; 120 minutes; 1; 4 and 7 days, respectively. The beads were characterised by elemental composition, thermogravimetric analysis (TG-DSC) and scanning electron microscopy (SEM-EDX). In order to perform the morphological analysis, the beads were freeze-dried (pressure of 0.060 mmHg for 72 h), therefore the qualitative and quantitative composition of the beads is not altered during drying. The beads keep their shape and collapse of the structure is prevented, so that the micrographs can show their internal structure. The results clearly show the internal cavities formed. Semi-quantitative analysis shows that the bead surface has a higher percentage of carbon from alginate. The interior has a higher percentage of aluminium and silicon from montmorillonite. These analyses show that Mt is mainly located inside the bead. After beads characterisation, the adsorption of PQ as a function of time was studied for 3 initial concentrations of the herbicide (C_0 = 19, 38 and 50 ppm) on the beads with gelation times of 30 minutes and 7 days. The experiments were carried out by contacting the PQ with the materials with constant stirring, then 4 mL of solution were withdrawn at set times, the PQ in that solution was quantified and then the volume was returned to keep the adsorbate/adsorbate ratio constant. All experiments were carried out at room temperature (25 ± 1°C) and 1×10^{-2} M NaCl ionic strength. Kinetics adsorption studies were also carried out using alginate beads without montmorillonite (Alg-Mt0). The PQ was spectrophotometrically quantify by UV/vis at 257 nm. Adsorption isotherms were obtained by performing batch adsorption experiments. For that, Alg-Mt70 composites beads were placed in polypropylene centrifuge tubes. After that proper volumes of 1×10^{-2} M NaCl and appropriate aliquots of stock solution of PQ were added to cover concentration ranges from 5.0×10^{-5} to 3.0×10^{-3} M. The pH was 5.5 ± 0.2 in all experiments. The tubes were shaken enough time for it to reach equilibrium. All experiments were carried out at room temperature (25 ± 1 ºC). The experimental results of herbicide adsorption as a function of time were fitted with the Shrinking Core Model (SCM) [2]. The concentration profile as a function of time was obtained. The results obtained showed a very good agreement between the model prediction and the experimental data. The effective diffusion coefficients of the adsorbent material were obtained as fitting parameters. No major differences were observed in the adsorption behaviour with the gelation time of the beads, so it can be concluded that Alg-Mt70 beads with only 30 minutes in $CaCl_2$ is a stable and efficient material for PQ adsorption, not requiring long gelation processes.

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Removal of caffeine from water sources using alginate/carbon nanotubes beads

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According to the United States Environmental Protection Agency (USEPA), emerging contaminants are defined as chemical compounds that can enter the environment with human health impacts that are still unknown[1]. Caffeine (CF) is a psychoactive substance widely consumed both, in naturally occurring products such as tea, coffee, cocoa, and in artificial products, such as energy drinks. It is also used as active ingredient of pharmaceuticals of massive used. The synthesis of new materials for CF adsorption/desorption is of great interest for its removal from water sources. There are some reports about the use of carbonaceous solid materials in combination with the biopolymer alginate in pollutant removal studies[2], but its application in columns is scarce. In this sense, the present work proposes the synthesis and characterization of alginate/carbon nanotubes (AB/NTCs) composite beads and the implementation of these materials in an adsorption/desorption minicolumn for the removal of CF.

For the synthesis of the AB/NTCs, a suspension was prepared by dispersing the NTCs in 1% w/v deionized water using ultrasound for 2 h. At the same time, a solution containing 1% w/v alginate in deionized water was prepared and kept under constant stirring for 2 h. After homogenization of the alginate, the NTCs suspension was added. The beads were formed in a 0.1 M calcium chloride solution. The beads were characterized by scanning electron microscopy, digital photography, and infrared spectroscopy. A simple automated system was designed to carry out the adsorption and desorption of CF. For this, beads were packed in a minicolumn (3.0 x 0.5 cm i.d.). A 1 mg L^{-1} solution of CF was passed through the minicolumn at a flow rate of 0.50 mL min^{-1}, and then acetonitrile was used to perform the desorption. Quantification of CF was performed by UV-Vis. These conditions indicate that it is possible to use the AB/NTCs composite packed in a minicolumn as a model for CF retention, quantification, and subsequent desorption of the sample to recover the original material.

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Use of mosses for heavy metals removal from the environmental

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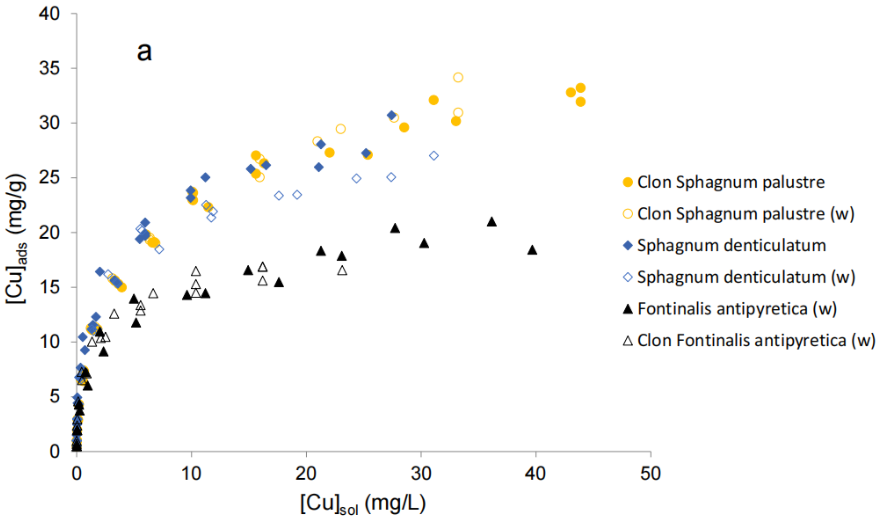
It has been proven that mosses, due to their specific characteristics, possess high capacity for metal retention, which makes them potential biomonitors of environmental pollution. In order to establish comparisons between different species, laboratory production of mosses and clonation have proliferated.

Furthermore, these species can be also used to control pollution of natural waters. The removal of metals from solution can happen through different mechanisms since the metal can be bound to the surface sites of the moss (sorption) or can form complexes with soluble organic matter. In this work, we have analysed different factors that can affect the retention of Cu, Cd and Pb by the moss: the species, use of clons or natural species, pre-treatment of the mosses (i.e. washing (w) and demethylation), pH, etc.

Acid-base titrations of the mosses were conducted to determine the point of zero charge and to quantify the potential binding sites available for metal binding. Due to the heterogeneous nature of the functional groups (e.g. carboxyl, phosphoryl, phenol, amine, etc.) present in mosses, a bimodal distribution model was used to obtain de log K and abundance of the sites. Also, adsorption experiments of three metal cations, were conducted at constant (isotherms) and variable pH (adsorption edge). From the isotherms (Figure 1a) we can conclude that the affinity sequence for Cu adsorption is: Clon Sphagnum palustre ~ clon Sphagnum palustre (w) ~ Sphagnum denticulatum > Sphagnum denticulatum (w) > Fontynalis antipyretica (w) ~ clon Fontinalis antipyretica (w). The fitting of different isotherm equations to the experimental data showed that the adsorption behaviour is better explaind by a Langmuir-Freundlich isotherm (Figure 1b).



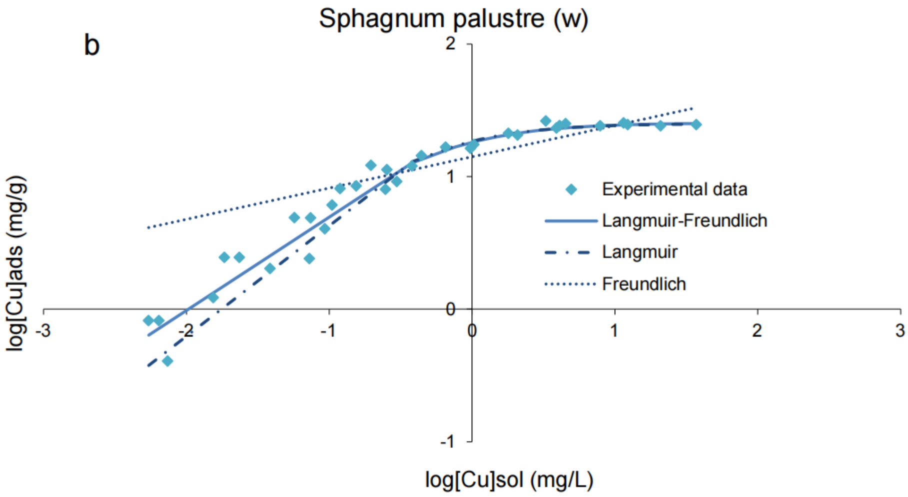


Figure 1: a) Copper adsorption on different species of moss. ((w) is used for washed mosses) b) Fitting of the Langmuir Freundlich isotherm to the experimental data (log-log scale).

Adsorption edges were obtained at different metal concentrations for the species Fontinalis antipyretica (natural and cloned) and their demethylated forms. The use of the demethylated forms from either the moss or its clon led to an important increase in Cd adsorption, although no such improvement was observed for Cu retention.

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Mesoporous silica: Is it really effective for decontamination of water bodies?

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Introduction

It is known that the benefits offered by mesoporous silica (SiO_2) such as being stable, innocuous, with high surface area and pore size, etc., make it attractive in a wide variety of technological, scientific, and medical applications. In addition, the surface of this solid can be modified / functionalized with different chemical substances, expanding its use and improving its selectivity. In the case of its application as adsorbent in water, our group has been working for a decade with mesoporous SiO_2 in order to evaluate under what conditions and with what species these materials result effective. This work presents a study of the adsorption capacity of mesoporous SiO_2 in water, with and without organic and inorganic linkers, towards cationic (paraquat PQ^{2+} and malachite green MG), polar / zwitterionic (norfloxacin NFX, doxycycline DXC), and anionic (methyl orange MO and 2,4-D) species in order to compare their performance, with that of the other adsorbents reported in literature. Finally, regeneration of the adsorbent and reuse (crucial parameter to be evaluated from the technology point of view) studies were also carried out and are discussed[1].

Results

Adsorption isotherms showed that SiO_2 is highly effective towards the adsorption of PQ^{2+} and MG being better than most materials (natural and synthetic) reported in the literature. This desired behavior is maintained after several cycles of reuse, and the adsorption is the result of electrostatic attractions between adsorbates and deprotonated silanol groups of the surface. On the contrary, the adsorption capacity decreases dramatically with zwitterionic and anionic molecules, in the latter being negligible. In the case of DXC, the presence of Ca^{2+} ions significantly increases the affinity of the adsorbate for the surface because the divalent cation acts as a bridge between DXC and SiO_2. In the case of the anionic MO and 2,4-D species, APTES ($-Si-C_3H_6-NH_2$) molecules anchored on the surface of SiO_2, reverses the negative charge of the solid in aqueous medium (IEP≈7.8) and facilitating the adsorption of the the pollutants by electrostatic attractions. Although the reuse capacity remains very high in the PQ^{2+} (and NFX)-SiO_2 systems, it strongly decreases in MO-APTES-SiO_2 system due to the partial hydrolysis of the linker, which regenerates the silanol groups.

Conclusions

Mesoporous SiO_2 shows a great adsorption capacity for cationic species, with the possibility of reusing it on several occasions. In the case of zwitterionic and anionic contaminants, the silica surface must be modified with appropriate molecules or ions in order to obtain acceptable removal of the adsorbates. The chemical stability of the linker is a crucial point to take into account when functionalizing the adsorbent.

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P15

The role of mineral structure in metal speciation and cycling in contamined soil

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Birnessites are a variety of hydrous-layered manganese oxides (phyllomanganate) in natural environments and known as the scavenger of heavy metal in nature. Birnessites possess an external and an interlayer surface that are both available for ion adsorption. However, the level of quantitative understanding of metal ion adsorption to birnessite as a function of the environmental conditions is still much smaller than that of metal ion binding to iron and aluminum (hydr)oxides. The main reason for this is that for the latter (hydr)oxides the multi-site surface complexation model including charge distribution (CD-MUSIC) developed by Hiemstra et al. has been worked out in combination with a Stern-Gouy-Chapman (SGC) model of an electrical double layer (EDL), whereas for birnessites only rather simple and not very realistic surface complexation models have been used. In addition, heavy metal adsorption onto birnessite was found to depend on the birnessite microstructure, including the absolute numbers of vacant sites, edge sites and the amount of Mn(III) in the interlayer and in the layer for birnessites with a different Mn average oxidation state (MnAOS). However, some controversy exists on contribution of vacant and edge sites to the total heavy metal adsorption. Therefore, using X-ray diffraction with Rietveld refinement to obtain the reactive sites and their densities, a CD-MUSIC model combined with a Stern-Gouy-Chapman electrical double layer (EDL) model for the external surface and a Donnan model for the interlayer surface is developed for birnessites with different Mn average oxidation state (MnAOS). Proton affinity constants and the charge distributions of Pb surface complexes were calculated *a priory*. By fitting Pb adsorption data to the model the obtained equilibrium constants ($\log K_{Pb}$) of Pb complexes were 6.9-10.9 for the double-corner-sharing and double-edge-sharing Pb^{2+} complexes on the edge sites and 2.2-6.5 for the triple-corner-sharing Pb^{2+} complex on the vacancies. The larger $\log K_{Pb}$ value was obtained for higher MnAOS. Speciation calculations showed that with increasing MnAOS from 3.67 to 3.92 the interlayer surface contribution to the total Pb^{2+} adsorption increased from 43.2% to 48.6%, and the vacancy contribution increased from 43.9% to 54.7%. The vacancy contribution from interlayer surface was predominant. The present CD-MUSIC-EDL model contributes to understand better the difference in metal adsorption mechanism between birnessite and iron/aluminum (hydr)oxides and is very useful for improving the accuracy of the risk assessment of heavy metal ion pollution in soils.

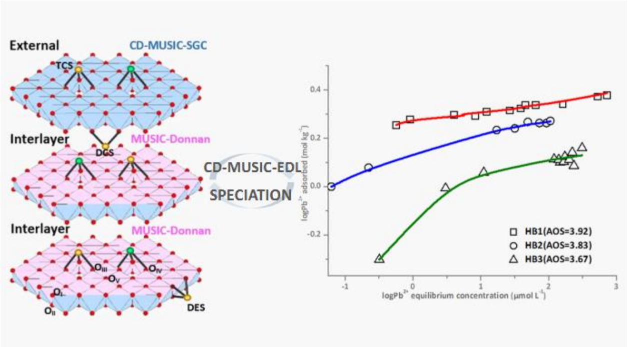

Figure 1: CD-MUSIC-EDL model for Pb adsorption on birnessite.

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Phosphate speciation on Al-substituted goethite: ATR-FTIR /2D-COS and CD-MUSIC modeling

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Natural goethite commonly encounters Al substitution for Fe, which alters the surface reactivity of goethite. Whether and how Al substitution affects the surface speciation of phosphate remains poorly understood. Therefore, the phosphate adsorption and speciation of Al-substituted (6 and 9 mol%) goethite were investigated by combining attenuated total reflectance Fourier transform infrared (ATR-FTIR) and CD-MUSIC modeling. Al substitution caused a decrease in crystal length-to-width ratio of goethite and the ratio of (110)/(021) faces was estimated to 90/10, 85/10 and 81/19 for goethite with about 0, 6 and 9 mol% Al, respectively. The decreasing (110)/(021) face ratio and increasing surface roughness with increasing Al substitution enhanced the surface charge density and phosphate adsorption capacity of goethite. Two-dimensional correlation spectroscopic (2D-COS) analysis showed that three types of phosphate complexes were formed on both pure and Al-substituted goethites. CD-MUSIC modeling, based on electron microscopy and ATR-FTIR results to arrive at part of the parameters, could describe both the proton and phosphate adsorption well with optimized remaining parameters. The model parameters indicated that Al substitution in goethite led to larger affinity constants for bidentate phosphate complexes and smaller values for monodentate complexes. Therefore, a larger percentage of bidentate phosphate complexes were formed on Al-substituted goethite than on pure goethite. Monodentate phosphate complexes were hardly formed on the Al sites of Al-substituted goethite (Figure 1). The results improve our insight regarding phosphate binding to Al-substituted goethite and the phosphorus availability and mobility in iron-rich soils.

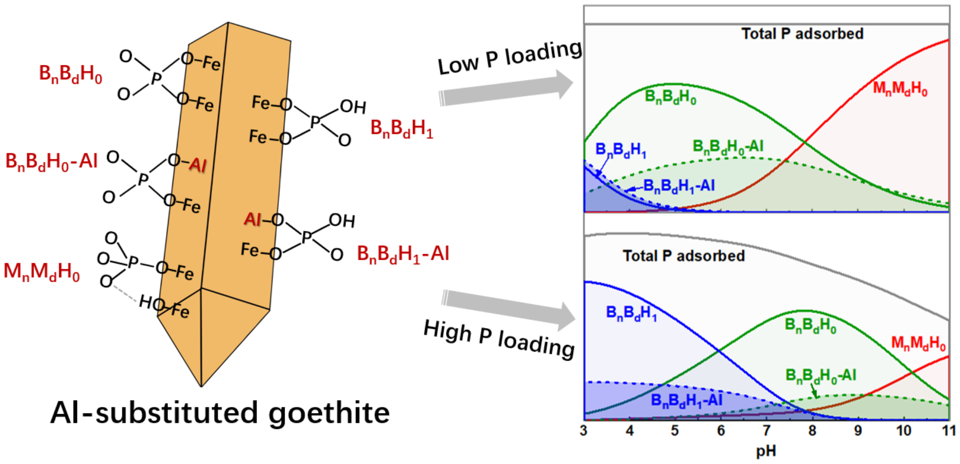

Figure 1: The phosphate speciation adsorbed on the Al-substituted goethite as a function of pH calculated with CD-MUSIC model.

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Selective and quantitative adsorption mechanisms of soil humic substance on multi-component minerals

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The stabilization and preservation of soil organic matter have been attributed to the strong reactive sites of mineral surfaces that cause physical isolation and chemical stabilization due to the organic-mineral interface. The interaction processes between organic matter and minerals interface still remains poorly understood due to limit of the obtaining of quantitative information of the interaction. This study used micro-scale knowledge (including two-dimensional FTIR Correlation Spectroscopy (2D-FTIRCoS), isothermal titration calorimetry (ITC) and X-ray Photoelectron Spectroscopy (XPS)) to directly measure the binding processes of humic substances (HSs) groups onto clay minerals surfaces. And thus, the qualitative and quantitative information about the interaction processes were revealed. The spectroscopy results showed that the carboxylate groups, aliphatic OH and aromatic structure participate in the binding of HA (humic acid) on kaolinite surface. The carboxylic and phenolic hydroxyl interact with kaolinite surface through the interfacial C\\O\\Al/Si bonds. Kaolinite prefers to adsorb C-groups at pH 4.0 and O-groups at pH 8.0. The interaction of COO^- group leads to the formation of inner-sphere complex first and then outer-sphere complex with increasing contact time. The interaction of COOH group with the $AlOH_2^+$ of kaolinite was could be ascribed to ligand exchange and/or electrostatic attraction, whose contribution was evaluated to be 13.90%, 7.65% and 0% at pH 4.0, 6.0 and 8.0, respectively. These results of molecular binding provide quantitative mechanistic insights into organic-mineral interactions and expound the effect of functional groups of HA on binding mechanisms, and thus bring important clues for better understanding the mobility and transformation of land-carbon including mineral-bound carbon.

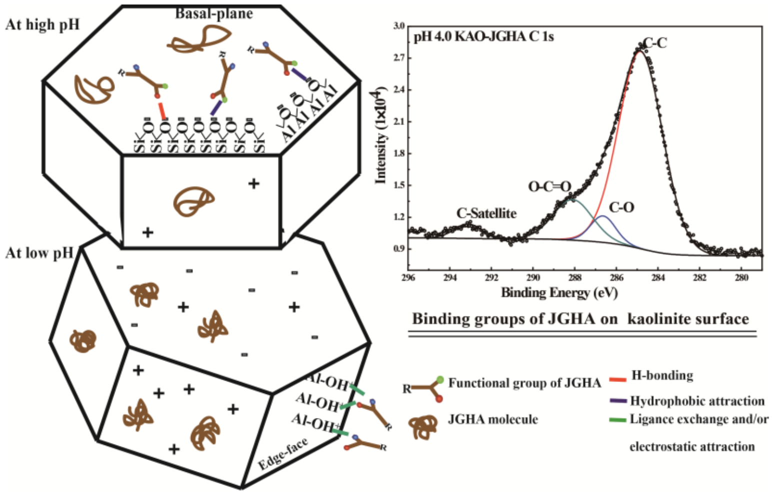

***Figure 1:** The **quantitative** distribution of HA groups on kaolinite/water interface*

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Fraction distribution of heavy metals and its relationship with iron in polluted farmland soils around distinct mining areas

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Polluted farmland soils around mining areas are usually enriched in Fe (oxyhydr)oxides and various heavy metals (HMs), however, their interactions, essential to evaluate the mobility and availability of HMs, in such soils are poorly understood. In this study, HMs polluted farmland soils were collected from several typical mining areas distributed from the south to the center of China, with distinct soil physicochemical properties. We comparatively analyzed the chemical fractions of HMs and Fe in these soils and determined the association relationship between HMs and Fe fractions using chemical extraction and correlation analysis. Most soils contain multiple HMs like As, Cu, Pb, Zn, and Cd, with varying environmental risks across the regions. Excluding the residual fraction, Cu, Pb, and Cd mainly exist in the reducible fraction, while Zn predominately accumulates in the oxidizable fraction. The total Cu, Pb, and Zn exhibit positive correlations with their available contents ($P < 0.01$), suggesting that the availability of these HMs is predictable by their total contents. Additionally, the positive correlations among Pb, Zn and Cd indicate that these HMs are associated with each other. Arsenic in these soils is predominantly associated with various Fe fractions, while Cd shows a closer relationship with crystalline Fe oxides and probably locates in the mineral structure. Additionally, As and Cd exhibit significant positive correlations within various Fe oxides, suggesting a synergistic accumulation effect in these soils. These new insights into the fraction distribution of HMs and their association properties with Fe fractions are essential to ecological risk assessment and remediation of HMs in polluted farmland soils.

Facet-dependent surface charge and Pb^{2+} adsorption characteristics of hematite nanoparticles: CD-MUSIC-eSGC modelling

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Accurate prediction of the environmental fate of Pb depends on the understanding of Pb coordination to mineral surfaces. Here, the proton and Pb adsorption and speciation on hematite nanocrystals with different exposed crystallographic facets were investigated. High-resolution transmission electron microscopy images revealed that hematite nanoplates (HNP) were of 75.3 ± 9.5% (001) facets and 24.6 ± 9.3% (012) facets, while hematite nanocubes (HNC) were of 76.0 ± 11.1% (012) facets and 24.0 ± 3.2% (110) facets. Our modeling results revealed that the proton affinity constant (log K_H) of $\equiv FeOH^{-0.5}$ and $\equiv Fe_3O^{-0.5}$ was 7.8 and 10.8 on hematite (012) facets, and changed to 7.7 and 11.7 on (110) facets, respectively. Owing to the different atomic arrangements, (012) facets not only have higher adsorption performance for Pb, but also present a greater dependence on pH than (110) facets. Additionally, our modeling further indicated that (012) facets bind Pb via both bidentate and tridentate complexes, while (110) facets bind Pb only through bidentate complexes at pH 3.0-6.5. These results facilitate a more detailed understanding of the complex species of Pb on hematite surface while also provide new insight into the reactivity mechanism of individual hematite facets.

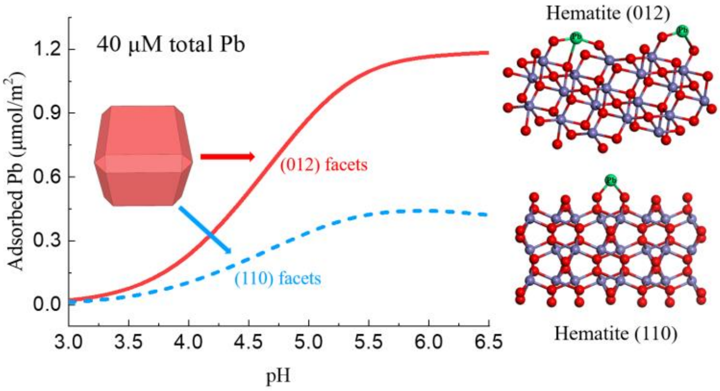

Figure 1: Adsorption performance of Pb on (012) facets were higher than that on (110) facets.

Acknowledgements

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Impact of low-molecular-weight organic acids on selenite immobilization by goethite: Understanding a competitive-synergistic coupling effect and speciation transformation

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The interactions between low-molecular-weight organic acids (LMWOAs) and selenium (Se) on mineral/water interfaces affect the release, immobilization and bioavailability of Se in nature. Herein, the effects of three environmentally relevant LMWOAs (i.e., oxalic (Oxa), succinic (Suc) and citric (Cit) acids) on Se(IV) adsorption to goethite under oxic conditions were investigated using batch experiments, speciation fractionation, and ATR-FTIR and XPS analyses. The LMWOAs exhibited a competitive-synergistic coupling effect on Se(IV) adsorption to goethite, which inhibited the adsorption rate of Se(IV). However, immobilization of Se(IV) was simultaneously enhanced in the following order: Oxa > Suc > Cit. The results obtained by fractionation of the adsorbed Se(IV) revealed that the enhancement was due to surface binding as well as speciation transformation from ligand-exchangeable Se(IV) into residual fractions, which increased by approximately 18% in the presence of the LMWOAs. The dissolution of goethite significantly improved due to the LMWOAs and decreased to different degrees as the concentration of Se(IV) increased.

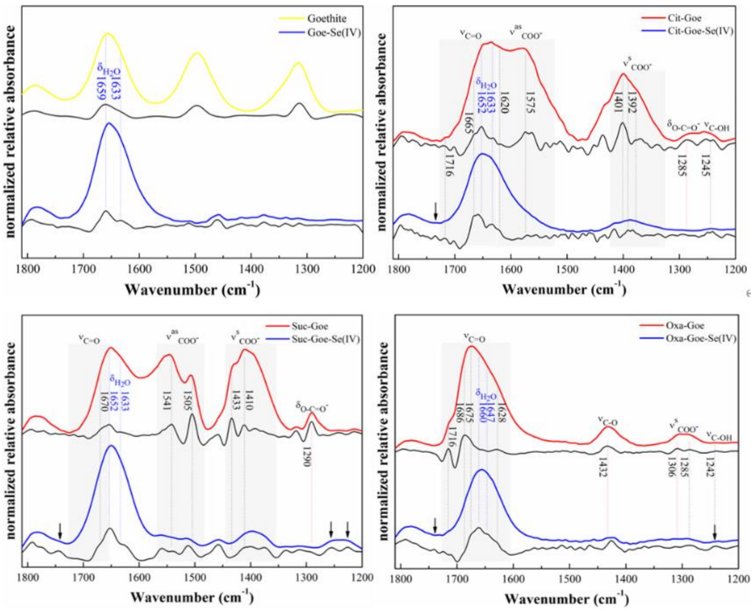

Fig. 1. ATR-FTIR spectra (1800–1200 cm^{-1}) of freshly synthesized goethite and solids after reaction at pH 5.0: yellow line represents the freshly synthesized goethite; blue lines illustrate the solids after reaction between goethite and Se(IV) (1.9 mmol L^{-1}) at pH 5.0 in the presence of 1 mmol L^{-1} LMWOAs. Red lines represent the solids after reaction between goethite and 1 mmol L^{-1} LMWOAs only. Black lines illustrate the corresponding negative second derivative spectra.

Modifying MIL-100(Fe) through co-growing iron oxides to enhance its adsorption for selenite

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Composite materials of MIL-100(Fe) combined with akaganeite and hematite (MIL-100(Fe)@Aka and MIL-100(Fe)@Hem) were prepared by co-growing iron oxides with MIL-100(Fe) in-situ under hydrothermal solutions. Compared with the MIL-100(Fe), MIL-100(Fe)@Aka possessed the more stable surface charge in the range of pH 3.0-8.0, and MIL-100(Fe)@Hem displayed the higher density of active sites. Both MIL-100(Fe)@Aka and MIL-100(Fe)@Hem exhibited the spontaneous and exothermal adsorption process for Selenite (Se(Ⅳ)), which can be well described by the pseudo second-order-rate model. Adsorption capacities suggested that there was an obvious synergistic effect on the adsorption of Se(Ⅳ) by the MIL-100(Fe)@Aka and MIL-100(Fe)@Hem. The maximum enhanced coefficient of 154% and 153% can be realized respectively by the introduction of akaganeite and hematite into MIL-100(Fe). Saturated adsorption capacity of MIL-100(Fe)@Hem$_{0.1}$ fitted by Sips model was very high (301.93 mg/g).

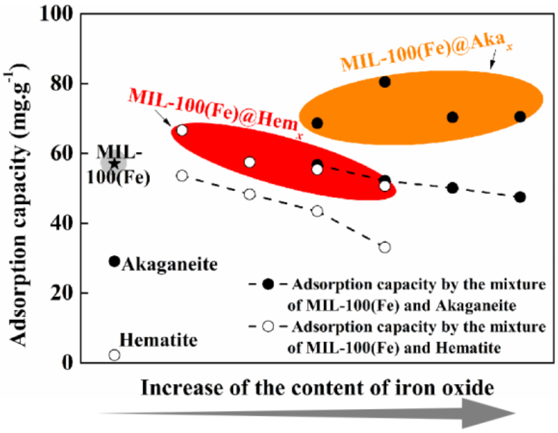

Fig. 1 Selenite adsorption capacities of the samples

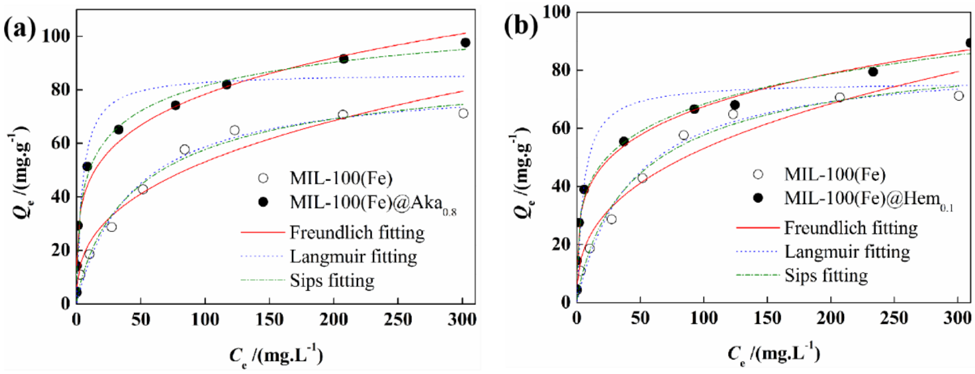

Fig. 2 Adsorption isotherms of selenite on MIL-100(Fe), MIL-100(Fe)@Aka$_{0.8}$ and MIL-100(Fe)@Hem$_{0.1}$

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