



**Politecnico
di Torino**

Department of Environment,
Land and Infrastructure
Engineering



Interfaces
Against
Pollution

POLITECNICO DI TORINO
SEPTEMBER 15-18, 2024

BOOK OF ABSTRACT

INTERFACES AGAINST POLLUTION





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INTERFACES AGAINST POLLUTION

TORINO 2024



WEBSITE

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CONTACTS

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IAP | INTERFACES AGAINST POLLUTION

ABOUT IAP

IAP conferences seek to provide a forum for researchers working in the interdisciplinary field of Environmental Science and Environmental Engineering, the main focus of their work being the importance of (bio)colloids and (bio)interfaces in natural and engineering processes, both from fundamental and applied perspectives.

The scope includes topics of societal concern such as environmental protection, water decontamination, (bio)remediation of polluted sites, optimisation of mineral resources, impacts of nanotechnology on the environment, and the key role played by interfaces in governing the fate and behavior of pollutants in the environment. An adequate investigation of these matters necessarily requires joint experimental and theoretical expertise from physicists, physical chemists, chemists, biologists, geoscientists, and engineers.

HISTORY OF IAP

The first conference with the name Interfaces Against Pollution took place in Wageningen, The Netherlands, in 1997. To date, 10 IAP conferences have taken place at locations across Europe and Asia. The first IAP conference was organised within the auspices of the IUPAC Commission of Colloid and Surface Chemistry, and IUPAC's history of involvement in conferences on Colloids and Surfaces in the Environment dates back to 1992. Prior to establishment of the IAP series, IUPAC organised several conferences in this general domain:

- **Colloids in the Aquatic Environment**, 7-9 September 1992, London, UK. Chair: John Gregory (University College London). Proceedings published in *Colloids and Surfaces A*, 1993, vol. 73
- **Surface and Colloid Science and its Relevance to Soil Pollution**, March 1994, Madras, India
- **International Forum on Environmental Catalysis**, 25-27 October 1995, Tokyo, Japan. Chair Matsumoto Misono (University of Tokyo). Proceedings published in *Catalysis Today*, 1997, vol. 35 (1-2)
- IUPAC/ICSU workshop on **Electrochemistry and Interfacial Chemistry in Environmental Clean-up and Green Chemical Processes**, 6-7 April 2001, Coimbra, Portugal. Chair: Christopher Brett (University of Coimbra); Co-chairs: James F. Rusling (University of Connecticut, US), Luuk Koopal (Wageningen University, NL) & John Gregory (University College London, UK). Proceedings published in *Pure and Applied Chemistry*, 2001, vol. 73 (12)

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The International Advisory Council oversees and supports the IAP conference series to ensure its continuity at a high scientific level.

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PAST IAP CONFERENCES

Interfaces Against Pollution 2024 in Torino marks the 13th edition of the conference and follows the previous ones held since 1997:

IAP2022, 18-21 September, Antwerpen, BE

IAP2021, 14-17 May, Wuhan, CN

IAP2018, 10-13 June, La Grande Motte, FR

IAP2016, 4-7 September, Lleida, ES

IAP2014, 25-28 May, Leeuwarden, NL

IAP2012, 11-14 June, Nancy, FR

IAP2010, 16-19 May, Beijing, CN

IAP2008, 1-4 June, Kyoto, JP

IAP2006, 4-7 June, Granada, ES

IAP2004, 24-27 May, Jülich, DE

IAP2002, 27-30 May, Miskolc, HU

IAP1997, 10-13 August, Wageningen, NL

SCIENTIFIC AND SOCIAL PROGRAMME

SUNDAY 15 SEPTEMBER	Politecnico di Torino, 10138 Torino, Central court (https://maps.app.goo.gl/qSW7UiWtPK4htiBZ7)	
17:30 – 19:15	Welcome reception	
MONDAY 16 SEPTEMBER	Politecnico di Torino, 10138 Torino, Room 10i adjacent to court (https://maps.app.goo.gl/qSW7UiWtPK4htiBZ7)	
8:30 – 9:00	Registration	
9:00 – 9:10	Opening of IAP2024	
9:10 – 10:15	Plenary: Prof. Christa McArdell, EAWAG, Switzerland “Advanced wastewater treatment to abate micropollutants: Switzerland as example for EU?” (*_0) Chair: Philippe Behra, Institut National Polytechnique de Toulouse, France	
	Politecnico di Torino, 10138 Torino (https://maps.app.goo.gl/qSW7UiWtPK4htiBZ7)	
10:15 – 10:50	Refreshment break and set up of posters (posters in Room 12i)	
	Room 8i (a) - Role of interfaces in pollutant dynamics	Room 10i (b) -Theory and Modeling of Interfaces and Interface Phenomena
10:50 - 11:30	Chair: Takumi Saito, The University of Tokyo, Japan Keynote: Prof. Monica Passananti – University of Helsinki, Finland; University of Turin, Italy “Study on multiphase degradation of plastic nanoparticles” (a4_0)	Chair: Yasuhisa Adachi, University of Tsukuba, Japan Keynote: Prof. Claire Chassagne – TU Delft, The Netherlands “Modeling flocculation” (b3_0)
11:30 – 11:50	Hou et al. - Huazhong Agricultural University, China The interfacial reaction hotspot in metastable iron minerals: the role and contribution to arsenic immobilization (a4_1)	Lesniewska et al. - Université de Lorraine-CNRS, France Conditional existence of Donnan potential in soft particles and surfaces: dependence on steric effects mediated by electrolyte ions and structural charges (b3_1)
11:50 – 12:10	Assaf et al. - Université Paris-Saclay, France Impact of mixed organic compounds on Ni(II) retention in clay rocks: Complexation and synergetic effects (a4_2)	Wang et al. – Université de Lorraine-CNRS, France Modelling trace metal binding to humic matter: presenting NICA-SPBT-PEST and discussing the validity of ‘generic’ parameters (b3_2)

Please note the following:

Plenary talk: 45 min + 15 min Q&A; Keynote: 30 min + 10 min Q&A; Regular talk: 15 min + 5 min Q&A

Also, note that presentations are indicated in this program with the name of the first author and his/her affiliation as reported in the related abstract. The first author may not necessarily be the presenter.

SCIENTIFIC AND SOCIAL PROGRAMME

MONDAY 16 SEPTEMBER

	Room 8i (a) - Role of interfaces in pollutant dynamics	Room 10i (b) -Theory and Modeling of Interfaces and Interface Phenomena
12:10 – 12:30	Wiersma et al. - Wageningen University and Research, The Netherlands How to measure and model cadmium availability in tropical soils for low-cadmium sustainable cacao? (a4_3)	Van Raffé et al. – Wageningen University and Research, The Netherlands Chromium(III) Binding to Purified Fulvic and Humic Acid and its Solid Solution Partitioning and Speciation in Soil (b3_3)
12:30 – 14:00	Lunch	
	Room 8i (a) - Role of interfaces in pollutant dynamics cont'd	Room 10i (b) - Theory and Modeling of Interfaces and Interface Phenomena cont'd
	Chair: Yael Mishaël, The Hebrew University of Jerusalem, Israel	Chair: Jérôme F.L. Duval, Université de Lorraine, France
14:00 – 14:20	Saito et al. - The University of Tokyo, Japan Hierarchical aggregation of humic nano colloids induced by metal ion binding by small-angle X-ray and neutron scattering (a4_4)	Borisover et al. – The Volcani Institute, Israel Does a Humic Model Disintegrate Upon Dilution? A Molecular Dynamics Simulation of Water Content Effects (b3_4)
14:20 – 14:40	Town et al. - Universiteit Antwerpen, Belgium Uptake/Release Kinetics of Metal Ions and Organic Molecules by Micro- and Nano-Plastics (a4_5)	Wulandari et al. – University of Tsukuba, Japan Application of standardized colloid mixing in terms of rate of coagulation to evaluate various types of flocculants in the early stages of flocculation (b3_5)
14:40 – 15:00	Pradel et al. - ETH Zurich, Switzerland Role of self-filtration in the deposition of fragments: the case of micro- and nanoplastics (a4_6)	Tsukanov et al. – The Hebrew University of Jerusalem, Israel Does It Slip? Water Flow at the Solid-Liquid Interface of Porous Media: Insights from Spectral Induced Polarization (b3_6)
15:00 – 15:20	Abid et al. - University of Turin, Italy Interface between polyethylene terephthalate microplastics and microbiota activity in the ruminal environment (a4_7)	Tan et al. – Huazhong Agricultural University, China Structural-controlled formation of nano-particle hematite and their removal performance for heavy metal ions (b3_7)
15:20 – 15:40	Van Hoef et al. - Wageningen University and Research, The Netherlands pH-dependent contaminant availability in relation to reactive surface (trans)formation during field scale sediment ripening (a4_8)	Gangal et al. – Wetsus, The Netherlands Modelling Biogenic Manganese and Iron Oxide Generation and Subsequent Removal of Organic Micropollutants (b3_8)
15:40 – 16:10	Refreshment break	

SCIENTIFIC AND SOCIAL PROGRAMME

MONDAY 16 SEPTEMBER	Room 8i (a) - Role of interfaces in pollutant dynamics cont'd	Room 10i (b) - Theory and Modeling of Interfaces and Interface Phenomena cont'd
16:10 – 16:30	Chair: Yael Mishael, The Hebrew University of Jerusalem, Israel Toda et al. - The University of Tokyo, Japan Interfacial reactions affecting the Cs leaching behaviors of adsorbents solidified with cement and geopolymer (a4_9)	Chair: Jérôme F.L. Duval, Université de Lorraine, France Dykstra et al. – Wageningen University and Research, The Netherlands Early breakthrough of activated carbon filters for PFAS removal: mechanisms and technology development (b3_9)
16:30 – 16:50	Schenkeveld et al. - Wageningen University and Research, The Netherlands Degradation of chrysotile asbestos in soil (a4_10)	Mortada et al. – Université de Reims Champagne-Ardenne, France Towards the use of mathematical models in predicting the retention of fluoroquinolones in soils (b3_10)
16:50 – 17:10	Huang et al. - Huazhong Agricultural University, China An in-situ method of SEM-EDS combined with image processing to evaluate the speciation and transformation of Cu and Pb in contaminated soil (a4_11)	Jin et al. – Huazhong Agricultural University, China Generic phosphate affinity constants of the CD-MUSIC-eSGC model to predict phosphate adsorption and dominant speciation on iron (hydr)oxides (b3_11)
17:10 – 18:00	Politecnico di Torino, 10138 Torino (https://maps.app.goo.gl/qSW7UiWtPK4htiBZ7) Poster session	
TUESDAY 17 SEPTEMBER	Room 8i (a) - Role of interfaces in pollutant dynamics cont'd	Room 10i (b) - Theory and Modeling of Interfaces and Interface Phenomena cont'd
9:00 – 9:20	Chair: Josep Galceran, University of Lleida, Spain Geysels et al. - Wageningen University and Research, The Netherlands Glyphosate speciation at the goethite interface: insights from surface complexation modelling and competition (a4_12)	Chair: David Waite, University of New South Wales Australia Keynote: Dr. Carlo Bianco – Politecnico di Torino, Italy Advanced nanoremediation processes for the effective removal of complex mixtures of persistent pollutants from groundwater (b2_0)
9:20 – 9:40	Peng et al. - Wageningen University and Research, The Netherlands PFOA and PFOS binding onto Goethite: Experimental results and modelling with the Charge Distribution and Multi-site Complexation (CD-MUSIC) Model (a4_13)	
9:40 – 10:00	Circelli et al. - University of Molise, Italy Microplastics identification in biosolids: application of NIR spectroscopy coupled with multivariate statistics (a4_14)	Nga Pham et al. – Université de Toulouse, France Study of the removal of copper by sorption onto lignocellulosic materials (b2_1)

SCIENTIFIC AND SOCIAL PROGRAMME

TUESDAY 17 SEPTEMBER

	Room 8i (a) - Role of interfaces in pollutant dynamics cont'd	Room 10i (b) - Theory and Modeling of Interfaces and Interface Phenomena cont'd
10:00 – 10:20	Antelo et al. - University of Santiago de Compostela, Spain Iron mineral surfaces and their impact on pollutant attenuation in acid mine drainage (a4_15)	Barreca et al. - University of Catania, Italy Reimagining the process of environmental remediation: An inventive "Up-and-Down" adsorption technique for eliminating Pyrene from acidic wastewater (b2_2)
10:20 – 10:50	Coffee break	
	Room 8i (a) - Advances in the characterization of interfaces and interface processes	Room 10i (b) - Interfaces Applied in Decontamination Systems cont'd
	Chair: Raewyn Town, University of Antwerp, Belgium	Chair: David Waite, University of New South Wales, Australia
10:50 – 11:10	Keynote 5: Prof. Eric Achterberg – Chemical Oceanography GEOMAR, Helmholtz Centre for Ocean Research Kiel, Germany	Gavriely et al. – Tel Aviv University, Israel Mucin-based Solutions for Water Decontamination (b2_3)
11:10 – 11:30	"New insights from the International GEOTRACES Programme on impacts of ocean boundaries and particle dynamics on ocean trace element biogeochemistry" (a5_0)	Benkhaled et al. – Institut Européen des Membranes, France Novel Biocompatible Trianglamine Networks for Efficient Iodine Capture (b2_4)
11:30 – 11:50	Tufenkji et al. – McGill University, Canada Advanced Methods to Detect and Image Microplastics and Nanoplastics in Whole Organisms (a5_1)	Baran et al. – Université Côte d'Azur, France Purification of metal-polluted water by a lavandin-based hydrochar (b2_5)
11:50 – 12:10	Anies et al. – Universiteit Antwerpen, Belgium In-situ application of the active-passive sampling (APS) technique for monitoring psychoactive compounds in wastewater (a5_2)	N'Gole et al. – Université Savoie Mont Blanc, France Nitrogen enriched activated carbons for the CO2 capture and separation (b2_6)
12:10 – 12:30	Gibeaux et al. – Université Savoie Mont Blanc, France Chitosan-based passive samplers for the analysis of norovirus in water by adsorption and desorption (a5_3)	Gallard et al. – Laboratoire de Chimie Agroindustrielle, Toulouse, France Phytosterols and lipids for methane capture (b2_7)
12:30 – 12:50	Li et al. – University of Montreal, Canada Extraction of inorganic nanoparticles from soils and their characterization by single particle ICP-MS (a5_4)	Szabo et al. – University of Szeged, Hungary Composite graphene oxide multilayers for nanofiltration of cationic pharmaceuticals (b2_8)
12:50 – 14:30	Lunch and poster session	

SCIENTIFIC AND SOCIAL PROGRAMME

TUESDAY 17 SEPTEMBER

	Room 8i (a) - Soil biogeochemistry and agriculture	Room 10i (b) - Interfaces Applied in Decontamination Systems cont'd
	Chair: Tiziana Tosco, Politecnico di Torino, Italy	Chair: Jerzy Zajac, University of Montpellier, France
14:30 – 14:50	Keynote: Prof. Renato Grillo – Sao Paulo State University, Brazil “Nano-enabled materials for sustainable agriculture” (a1_0)	Souifi et al. – University of Sfax, Tunisia Evaluation of porous carbon/CNTs Composite Membranes for Tannery Wastewater Treatment : Enhancing adsorption Efficiency through Membrane Filtration (b2_9)
14:50 – 15:10		Vione et al. – University of Turin, Italy Heterogeneous Fenton Processes for Water Treatment (b2_10)
15:10 – 15:30	Gassenbauer et al. – The Hebrew University of Jerusalem, Israel Insights into Environmentally Friendly Foliar Fertilization - Effect of Surfactant Dynamics on Zn²⁺ Penetration (a1_1)	Sciscenko et al. – University of Turin, Italy Optimization of the photocatalytic properties of g-C₃N₄ for environmental applications (b2_11)
15:30 – 15:50	Kou et al. – Huazhong Agricultural University, China Cadmium and Lead Interaction: A Model for Assessing Combined Heavy Metal Contamination in Soils for Food Safety Risk Evaluation (a1_2)	Waite et al. – University of New South Wales (UNSW), Australia; UNSW Centre for Transformational Environmental Technologies China Performance evaluation and optimization of a suspension-type reactor for use in heterogeneous catalytic ozonation (b2_12)
15:50 – 16:20	Refreshment Break	
	Room 8i (a) - Soil biogeochemistry and agriculture cont'd	Room 10i (b) - Interfaces Applied in Decontamination Systems cont'd
	Chair: Tiziana Tosco, Politecnico di Torino, Italy	Chair: Jerzy Zajac, University of Montpellier, France
16:20 – 16:40	Yabuki et al. – University of Lleida, Spain Availability and Desorption Kinetics of Phosphorus in Soils (a1_3)	Farinelli et al. – Institut Européen des Membranes, France Chitosan-based reactive surface for disinfection and contaminants degradation (b2_13)
16:40 – 17:00	Beceiro-Cillero et al. – University of Santiago de Compostela, Spain Abiotic reduction of nitrate by iron oxides and organic acids precursors (a1_4)	Saija et al. – Politecnico di Torino, Italy Adsorption-based water desalination: A bench scale performance evaluation (b2_14)
17:00 – 17:20	Forini et al. – São Paulo State University, Brazil Magnetic hybrid supraparticles: a novel strategic design for controlled release of agrochemicals (a1_5)	Eder et al. – University of Amsterdam, The Netherlands Designing a Nature-inspired Engineering Tool to Address Soil Pollution (b2_15)

SCIENTIFIC AND SOCIAL PROGRAMME

TUESDAY 17 SEPTEMBER

Room 8i (a) -
Soil biogeochemistry and agriculture cont'd

Room 10i (b) - Interfaces Applied in
Decontamination Systems cont'd

17:20 – 17:40

Dayan et al. – The Hebrew University of
Jerusalem, Israel
**Polysaccharide-Coated Apatite Formulations:
Enhanced Crop P-Uptake and Reduced
Leaching (a1_6)**

Longobardi et al. – Università degli studi del
Molise, Italy
**Use of biochar to remediate two different soils
polluted by Pb and As (b2_16)**

17:40 – 19:40

Meeting of the Board of IAP (only for Board members)

Mercato Centrale, 10152 Torino
(<https://maps.app.goo.gl/NQYbu8ohfVakG1eg6>)

20:00 – 23:00

Social dinner

WEDNESDAY 18 SEPTEMBER

Room 8i (a) -
Soil biogeochemistry and agriculture cont'd

Room 10i (b) - Interfaces Applied
in Decontamination Systems cont'd

9:00 – 9:20

Chair: Wenfeng Tan, Huazhong Agricultural
University, China

Akhdar et al. – Institut Charles Gerhardt de
Montpellier CNRS, France
**Calorimetric screening of microbial activity in a
model condition of soil contamination (a1_7)**

Chair: Marco Minella, University of Turin, Italy

Nguyen et al. – Saigon University, Vietnam
**Revolving Algae Biofilm: An emerging
green technology for wastewater treatment
and biomass production (b2_17)**

9:20 – 9:40

Wiersma et al. – Wageningen University &
Research, The Netherlands
**Quantifying the accuracy, uncertainty and
sensitivity of soil geochemical multi-surface
models (a1_8)**

Raval et al. – Université Savoie Mont Blanc,
France
**Activated carbons with supported magnetic
particles for the removal of micropollutants
from wastewater (b2_18)**

9:40 – 10:00

Marchetti et al. – University of Perugia, Italy
**Metals and metalloids uptake and translocation
in Phragmites australis specimens (a1_9)**

Le Thi et al. – Université Côte d'Azur, France
**Electromigration to remove phosphate ions
from an aquaculture pond by adsorption
(b2_19)**

10:00 – 10:40

Refreshment break

Politecnico di Torino, 10138 Torino, Room 10i adjacent to court
(<https://maps.app.goo.gl/qSW7UiWtPK4htiBZ7>)

10:40 – 11:45

Plenary:
**Prof. Andrew Utada, University of Tsukuba, Japan “Oil-eating bacteria are more efficient lying
down” (*_1) Chair: Alberto Tiraferri, Politecnico di Torino, Italy**

11:45 – 12:00

Closing of IAP 2024

Politecnico di Torino, 10138 Torino, Central court
(<https://maps.app.goo.gl/qSW7UiWtPK4htiBZ7>)

12:00 – 14:00

Lunch to stay or to go

POSTER LIST

Please note that presentations are indicated in this program with the name of the first author and his/her affiliation as reported in the related abstract. The first author may not necessarily be the presenter.

Poster sessions in Room 12i:

- Monday, September 16, 10:15 – 10:50, set up of posters
- Monday, September 16, 17:10 – 18:00, poster session #1
- Tuesday, September 17, 12:50 – 14:30, poster session #2 (with lunch)

(c1_1) Bertozzi et al., Politecnico di Torino, Italy – Valorization of spent coffee grounds as soil amendment and valuable bio-additives

(c1_2) Forini et al., São Paulo State University, Brazil – Supraparticles as a controlled release for fertilizers: synthesis, characterization, and fate in soil columns

(c1_3) Qin et al., Crops Research Centre, Teagasc, Ireland – Unravelling Soil Chemical Changes during Cd Remediation with Lime, Zn and Spent Mushroom Compost (SMC) in Potato-cultivated Soils

(c2_1) Craveri et al., Politecnico di Torino, Italy – Behavior of membrane distillation in the treatment of a diverse range of real and industrial water streams: challenges and future perspectives

(c2_2) Gyenes et al., University of Szeged, Hungary – Nanofiltration of positively charged caine type local anesthetics from wastewater: performance and selective removal

(c2_3) Meo et al., Politecnico di Torino, Italy – Enhancing Membrane Distillation for Water Desalination through Distributed Solar Radiation: A Numerical and Experimental Study

(c2_4) Pulido-Reyes et al., EAWAG, Switzerland – Assessment of Drinking Water Treatment Processes in Nanoplastics Removal: Pilot- scale and Modelling Studies

(c2_5) Pezzano et al., Politecnico di Torino, Italy – Laboratory measurement of saturated soil resistivity to assess the applicability of microbial electro-remediation in contaminated aquifers

(c2_6) Yang et al., Huazhong Agricultural University, China – Prediction of cadmium bioavailability in the rice-soil system on a county scale based on the multi-surface speciation model

(c2_7) Biscalchim et al., São Paulo State University, Brazil – Synthesis of magnetic beads based on alginate and chitosan for the removal of silver nanoparticles from aqueous solution

(c2_8) Sallakhniknezhad et al., Politecnico di Torino, Italy – Potable water recovery from representative aqueous solutions from lunar regolith via direct contact membrane distillation (DCMD)

(c2_9) Sheikhi et al., Politecnico di Torino, Italy – Performance Assessment of Filters Developed to Capture Microfibers Released during Laundering with Household Washing Machines

(c3_1) Morciano et al., Politecnico di Torino, Italy – Modeling mass and heat transfer mechanisms occurring across a hydrophobic membrane in Osmotic Membrane Distillation (OMD)

(c3_2) Xiong et al., Huazhong Agricultural University, China – Generic CD-MUSIC-eSGC model parameters to predict the surface reactivity of iron (hydr)oxides

(c4_1) Hering et al., Federal Institute for Geosciences and Natural Resources, Germany – Floating Iron Films as a Means for the Transport of Pollutants in an Abandoned Mine Drainage Tunnel in the Harz Mountains, Germany

(c4_2) Bhatkhande et al., University of Antwerp, Belgium – The effect of combined environmental stressors on *Daphnia magna* and *Brachionus calyciflorus*

(c4_3) Zihang et al., University of Tsukuba, Japan – Deposition Behavior of Cellulose Nanocrystal Particles through a Packed Alumina Beads across a Various pH Range

(c5_1) Sato et al., The University of Tokyo, Japan – Molecular characterization of reactive deep underground dissolved organic matters for metal ion using fluorescence spectroscopy and high-resolution mass spectrometry

(c5_2) Gibeaux et al., Université Savoie Mont Blanc, France – Passive sampler chitosan/activated carbon for norovirus analysis in water

(c5_3) David et al., Université Savoie Mont Blanc, France – Carbon materials for the passive sampling of soil gases

(c5_4) Maffei et al., Université de Lorraine, France – On the interpretation of the time-response of luminescent bacterial sensors for mechanistic evaluations of metal bioavailability and nanoparticle toxicity in aquatic media

ORAL PRESENTATIONS

Advanced wastewater treatment to abate micropollutants: Switzerland as example for EU?

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Keywords: micropollutants, wastewater treatment, ozonation, activated carbon, Swiss law

Abstract

Effluents from conventional wastewater treatment plants (WWTPs) are a major source of micropollutants (MPs), as they are not well removed in biological treatment. Swiss authorities have decided to implement additional wastewater treatment steps as mitigation strategy to improve water quality and to avoid potential negative ecological effects by MPs. A new water protection act entered into force on January 2016 which requires to upgrade selected WWTPs with advanced treatment to eliminate MPs by 80% from influent to effluent until 2040 (Eggen et al. 2014; FOEN law 2017). Treatment technologies are ozonation or sorption technologies with activated carbon, in powdered (PAC) or granular (GAC) form (Benstoem et al. 2017; Bourgin et al. 2018; Gulde et al. 2021). The financing of the advanced treatment is based on the polluters pay principle. The government introduced a wastewater tax for WWTPs which asks a fee of 9 CHF (about 9 Euro) per person and year. From this stock, 75% of the investment costs for the upgrade is paid. Overall, this results in an increase of costs for wastewater treatment of about 10-15%.

In this presentation, an overview will be given on the process and political approach that led to the upgrade of WWTPs and the new law. Technologies are presented that are implemented, including their benefits and challenges. Future developments in Switzerland are discussed concerning the upgrade of even more WWTPs. In the EU, a new urban wastewater treatment directive was proposed in 2022 which will most likely be approved in 2024. A similar approach to abate MPs is proposed as in Switzerland, but differences are related to the financing scheme.

Acknowledgments

Big thanks to many collaborators in divers project.

References

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- Gulde, R., Rutsch, M., Clerc, B., Schollée, J.E., von Gunten, U., McArdell, C.S. (2021) Formation of transformation products during ozonation of secondary wastewater effluent and their fate in post-treatment: From laboratory- to full-scale. *Water Res.*, 200,117200.

Oil-eating bacteria are more efficient lying down

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Keywords: biofilm; bacteria; oil-degrading; microfluidics; liquid crystal.

Abstract

Introduction

Nearly all known bacteria form social communities, called biofilms, which are dense cellular aggregates encased in a molecular glue that protects the community. Obligately hydrocarbonoclastic bacteria are a group of cosmopolitan marine bacteria that can survive by consuming hydrocarbons as sole carbon and energy sources. During oil spills they bloom to become the dominant bacteria at the site, where they form biofilms at the oil-water interface. It is known that these bacteria must adhere to the interface to use the oil, but the mechanism of oil consumption has been difficult to analyze.

Methodology

We introduce a microfluidic platform that allows the trapping and storage of oil microdroplets for weeks, while simultaneously enabling in situ cultivation of numerous oil-degrading biofilms; this greatly facilitates high-resolution imaging of the biofilm. Using the model oil-degrading bacterium *Alcanivorax borkumensis* (*Alca*), we present unresolved biofilm dynamics, showing its ability to rapidly consume oil by shredding the oil drops into wispy tube-like filaments (Fig. 1).

Results

We show that *Alca* modulates the local interfacial properties and correlate these changes to the ability of the cells to cooperatively drive a rapid and large-scale tubulation of the interface. Careful inspection of the rod-shaped cells at the oil-water interface reveals that they develop liquid crystal order and that interfacial tubulation emerges from aster-like topological defects in the nematic order.

The large drop deformation allows the biofilm to redistribute the oil to maximize the number of feeding cells, which ultimately maximizes consumption efficiency. Thus, we link the interfacial behavior of these bacteria with their ecological niche. Clarifying the microscopic mechanisms of biofilm formation for similar organisms may reveal features to be exploited in the management of oil spills and in oil recovery.

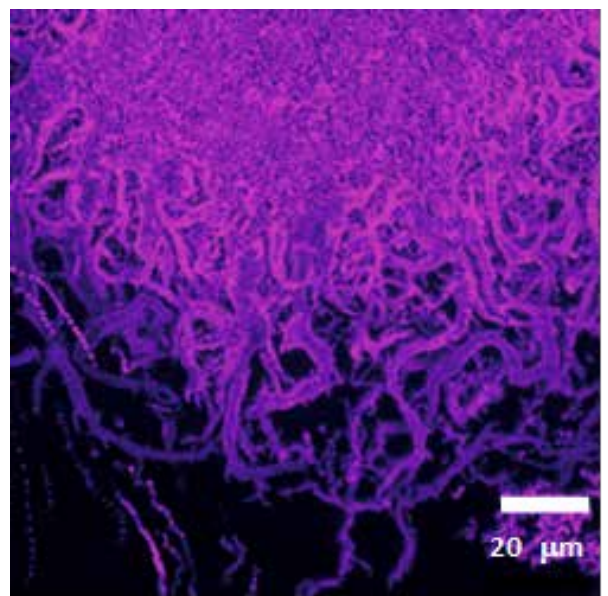


Fig. 1. Confocal image of bacteria-mediated interface tubulation. Cells constitutively express mCherry fluorescent protein (magenta)

Nano-enabled materials for sustainable agriculture

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Keywords: nano-enabled agriculture; controlled release; nanopesticides, nanofertilizers, sustainable agriculture.

Abstract

Ensuring food production in both quantity and quality to meet the demands of a growing global population is a significant challenge in the coming years. This challenge is further compounded by the urgent need to enhance the efficiency of conventional agricultural inputs, address the impacts of climate change, and bridge disparities in food access. Consequently, innovative, efficient, and ecologically sustainable approaches will be essential in the years ahead [1]. One promising avenue is the advancement of nano-enabled delivery systems for agrochemicals, which can improve the controlled release of active ingredients and provide protection against environmental biotic and abiotic stressors [2]. This talk will discuss the potential of nanopesticides and nanofertilizers to support environmentally friendly agriculture, offering a pathway to more sustainable and resilient food production systems.

Acknowledgments

This research was supported by FAPESP (#2022/03219-2 and #2023/00541-3), CNPq (#161360/2021-1), and CAPES (Finance Code 001).

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Insights into Environmental Friendly Foliar Fertilization - Effect of Surfactant Dynamics on Zn^{2+} Penetration

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Keywords: surfactant; contact angle; foliar fertilization; zinc

Abstract

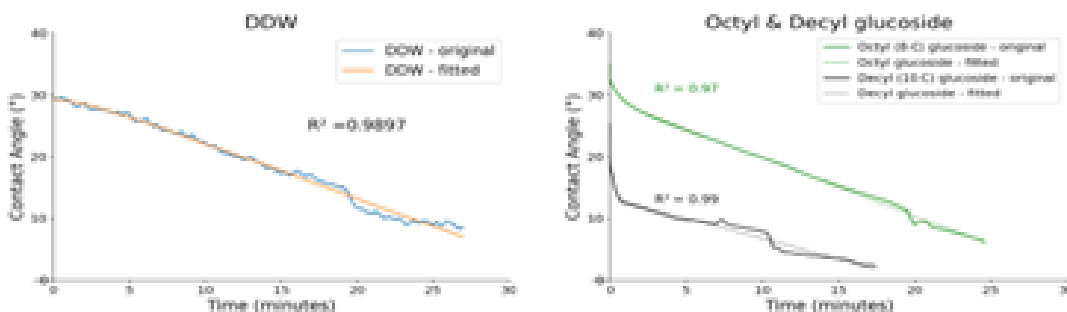


Figure 1. Contact angle change with time on glass substrate.

Foliar fertilization is a widely employed agricultural practice, yet fully understanding the mechanism of nutrient penetration into leaves, passing the exterior layer of the leaf, remains a challenge [1]. The hydrophilicity and the hydrophobic nature of the nutrient and leaf surface, respectively, inhibit droplet flattening, and therefore formulations include surfactants. Currently, an innovative formulation for foliar zinc was developed based on environmentally-friendly components; glucoside surfactant, decyl glucoside (DG), and poly-saccharide Zn^{2+} carrier, alginate. We hypothesized that as the length of the surfactant chain increases, surface tension decreases, which will enhance droplet flattening rate (decrease in contact angle with time) and therefore Zn^{2+} penetration will increase. Droplet dynamics, contact angle measurements with time on glass substrate (hydrophilic substrate) yield two empirical models: 1. $\theta = -at^2 - bt + c$ for control (no surfactant), which indicates a slow-flattening behavior. 2. $\theta = de^{-kt} - gt + f$ for surfactants with a chain length of 8 and 10, which indicates a fast-flattening behavior. Parameter k increases with surfactant chain length. These models 1 and 2 well fit water droplets on pepper leaves without and with surfactant, respectively.

Cadmium and Lead Interaction: A Model for Assessing Combined Heavy Metal Contamination in Soils for Food Safety Risk Evaluation

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Keywords: Heavy metal; Combined pollution; Interactions; Soil-plant system; Bioconcentration.

Abstract

Extensive research has delved into the toxicity and risks associated with individual heavy metals. While some studies have explored the combined toxicity of various heavy metals, there remains a pressing necessity to establish protocols for evaluating the combined contamination of heavy metal mixtures in relation to agricultural food safety risks. Here, we investigated the combined toxicity of cadmium (Cd) and lead (Pb) to *Oryza sativa* L. and *Triticum aestivum* L. root by hydroponic culture. The dose-dependent Cd-Pb interaction behaviors was analyzed with the concentration addition (CA) model, independent action (IA) model and mathematical statistical methods. The results of rice study showed that the interaction of Pb and Cd at similar concentrations showed a significant antagonistic effect on rice root elongation. At low Pb concentrations ($Cd > 0.0195$, $Pb < 0.015$ mg/L), there was a synergistic effect of the mixture on rice root; at high Pb concentrations ($Cd < 0.225$, $Pb \geq 1.25$ mg/L), Pb dominated the toxicity on rice root. The results of wheat study showed that the interaction behavior of Pb and Cd was significantly related to the dose of Cd. When Cd was < 0.002 or $0.021\text{--}0.061$ mg/L, the main interaction had an additive effect; and when Cd was $0.002\text{--}0.021$ or > 0.061 mg/L, the interaction had a significant antagonistic effect. We further established a Cd bioaccumulation model (BCF_{Cd} model) of wheat under the Pb-Cd combined pollution based on plant physiological characteristics. The effect of Pb stress on wheat BCF_{Cd} was quantitatively analyzed by the maximum and minimum enrichment coefficient (K_{max} and K_{min}). Application of the model to three distinct soil types demonstrated its robust performance in quantifying wheat root uptake ($R^2 = 0.84$) and grain uptake ($R^2 = 0.87$) of Cd. These results affirm the suitability of the BCF_{Cd} model for application within the context of the soil-wheat system. This robust predictive tool holds significant promise in establishing a comprehensive framework for evaluating food safety risk thresholds in the context of concurrent heavy metal contamination in soil environments.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 42277299, 32061123007) and Natural Science Foundation of Hubei Province, China (No. 2020CFA013).

Availability and Desorption Kinetics of Phosphorus in Soils

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Keywords: Diffusive equilibrium in thin films (DET); pore water; phosphorus availability; soil fertility.

Abstract

The global growth of crop production has largely been accomplished through the intensive use of pesticides and fertilizers that can cause severe contamination problems to soil and water bodies. Therefore, diagnosis, prediction and monitoring are key requirements for the management of soil nutrient reserves and the mitigation of harmful impacts on the environment [1].

Phosphorus (P) is one of the most heavily worldwide used and expensive fertilizers and the demand for P fertilizers is expected to increase in the next decades with a prediction of a global peak in P production around 2030 [2].

Prediction of phosphorus plant availability can be performed with conventional soil extraction methods (such as the Olsen method), but, due to the unique chemistry of P and its slow diffusion in soils, the quantification of available P is more difficult to determine [3]. The experimental techniques Diffusive Gradients in Thin-films (DGT) and Diffusive Equilibrium in Thin-films (DET) mimic diffusion/desorption in the soil which are key processes in plant root uptake [4]. Their results can be interpreted with existing models such as DGT-induced fluxes in soils (DIFS), new analytical solutions and new speciation codes that take into account the essential thermodynamic and kinetic processes in the soil.

In this study, DET and DGT devices have been deployed in three soils with different P content. The outputs have been compared and analyzed, taking into account complementary information (porewater concentration, Olsen extraction concentration, etc.), with the help of existing and newly developed theoretical tools that will be presented. The methodology can be used to better elucidate the behaviour of P diffusion kinetics and resupply capacity of P from the soil phase to solution and to the bioactive surface. These results should help to achieve a better management of P fertilization in a context of scarce resources while aiming at a decrease in P pollution.

Acknowledgments

This research received support from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 101034288, and from the Spanish Ministry of Science and Innovation (Projects PID2019-107033GB-C21, PID2020-117910GB-C21 and PID2022-140312NB-C21-C21) funded by MCIN/AEI/10.13039/501100011033.

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Abiotic reduction of nitrate by iron oxides and organic acids precursors

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Keywords: nitrate; reduction; iron oxides; eutrophication.

Abstract

Phosphorus (P) and nitrogen (N) are essential nutrients for plant growth, but their excessive application in agricultural soils can lead to leaching, resulting in elevated concentrations of these nutrients in aquatic systems. This causes the quality deterioration of both fresh and saline waters through eutrophication. Iron oxides have been extensively used to control the mobility and bioavailability of ions. However, organic matter can interact with iron oxides, affecting the mobility of these ions through competitive or synergistic interactions, altering surface charge and available sites on the mineral surface, and/or promoting redox processes.

In this study, we investigated how different iron precursors and the interaction with organic acids affects the mobility of N under varying environmental conditions, including pH, ionic strength, type of organic acid, and the presence of competing ions. The presence of organic acids and Fe(II) ions enhance the reductive process from nitrate to ammonium, although it may promote the mobility of other ions at relatively high pH. The reductive process is more efficient when amorphous iron oxides are selected, while the reduction is slowed down when iron zero valent particles are used as iron precursor. Our results indicated that changes in the nature of the organic component affect the elimination rate of nitrate.

The findings from this study were used to design remediation strategies to reduce the risk of eutrophication in water bodies. By understanding the mechanisms of organo-mineral interactions in removing phosphorus and nitrogen, we explored the potential to combine these composites with other common adsorbent materials, such as zero-valent iron (ZVI), biochar, and Technosols. The biogeochemical processes involved in phosphorus and nitrogen immobilization and/or transformation can be optimized under appropriate environmental conditions.

Acknowledgments

The work was supported by the Agencia Estatal de Innovación through the project EUTROSTOP (TED2021-131737B-I00) and by Xunta de Galicia - Consellería de Educación e Ordenación Universitaria (Consolidation of Competitive Research Groups; GI-1245, ED431C 2022/40)

Magnetic hybrid supraparticles: a novel strategic design for +controlled release of agrochemicals

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Keywords: supraparticles; nanoparticles; controlled release; sustainable agriculture

Abstract

Climate change and population growth have impacted agricultural production. By 2050, the world population could reach up to 10 billion people, implying an increase in the use of natural resources and a greater demand for food. Given this scenario, agrochemicals are used excessively and, as a result, they bioaccumulate in the soil and groundwater, presenting low efficiency. Nanotechnology is emerging as potential solution within the agricultural sector, with a focus on the development of more efficient and environmentally friendly materials for a controlled-release agrochemicals [1]. For instance, building blocks through self-assembly structures can be formed through the conjunction of colloidally dispersed nano-enabled materials, creating complex structures called supraparticles (SPs) [2]. Herein, hybrid SPs were manufactured using two types of nano-enabled agrochemicals: (i) magnetic nanoparticles coated with citrate (Fe_3O_4 @citrate NPs) as fertilizer and (ii) nanostructured lipid carriers containing the atrazine (CLN:ATZ) as herbicide. Thus, Hybrid SPs were fabricated using the evaporation-induced self-assembly method on a superhydrophobic surface with microcrystalline cellulose. SPs were characterized using several analytical techniques, and their in vitro release profile was assessed in aqueous media. Moreover, leaching tests were evaluated in soil columns. Scanning Electron Microscopy analyses coupled with Energy Dispersive Spectroscopy (SEM-EDS) and Stereoscopic Microscopy highlighted the morphology of the SPs and demonstrated the evaporation process of the hybrid SPs formation over time. Fourier Transform Infrared Spectroscopy (FTIR) showed evidence of the formation of SPs. Furthermore, the in vitro release kinetic analyses of iron ions and atrazine herbicide from the hybrid SPs revealed a slow release compared to individual nano-enabled agrochemicals. Additionally, leaching tests conducted in soil columns demonstrated that SPs remained longer at the surface, gradually releasing the active ingredients. Therefore, this hybrid system can be considered tri-functional, as it promotes the controlled release of micronutrients (e.g., iron) and herbicide (e.g., atrazine) while also providing magnetic properties to the system. Therefore, the development of hybrid supraparticles can represent an advancement for agrochemical release systems and contribute to safer and more sustainable agriculture.

Acknowledgments

This research was supported by FAPESP (#2022/03219-2, #2023/09217-4, #2023/00541-3, #2023/12087-5), CNPq (#161360/2021-1), and CAPES (Finance Code 001).

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Polysaccharide-Coated Apatite Formulations: Enhanced Crop P-Uptake and Reduced Leaching

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Keywords: phosphorous; nutrition; mucilage; soil-micorbiome.

Abstract

The necessity of enhancing phosphorous (P) availability to crops while decreasing its migration in the environment, is well known. We propose to coat apatite with biodegradable polymers for the design of novel phosphorous fertilizers. We hypothesise that the biodegradable coating will specifically stimulate Phosphate Solubilizing Bacteria (PSB) and general bacterial activity and consequently, reduce local pH and thereby enhance phosphorous availability. Apatite was coated successfully with mucilage, a natural polysaccharide, extracted from chia seed. Mucilage loadings reached up to 15%, and the coatings were stable upon rinsing with water. The formulations were applied in sandy soil and the CO₂ emissions (indicating microbial activity) of the samples contacting uncoated apatite and of a commercial fertilizer (Triple Superphosphate, TSP) were similar to the control. The highest CO₂ emissions were detected from the samples containing apatite coated with mucilage, suggesting high microbial activity. TSP leaching from the soil was 3 orders of magnitude higher than the leaching from the mucilage coated apatite. The effects of general soil bacteria and specific PSB on the local pH of an apatite medium, was demonstrated. In the presence of glucose, general soil bacteria and PSB reduced solution's pH by ~0.6 and 1-1.7 units, respectively, and the pH reduction directly correlated to enhanced apatite P solubility (fig. 1). A similar, but more moderate trend, was obtained for bacteria in the presence of mucilage. Wheat plants were grown in pots containing sandy soil treated with mucilage (Muci), apatite (Ap), apatite+mucilage (Ap+muci) and TSP. The dry weight of the wheat was significantly higher for the 'Ap+muci' treatment, followed by the plants treated with Ap or TSP, while the control and Muci treatments resulted in significantly low weight. Olsen measurements (P plant availability test) indicated higher P concentrations in the 'Ap+muci' treated soil. These results support our working hypothesis that application of the apatite formulation to the soil enhance microbial activity which induces phosphate release from bacterial populations.

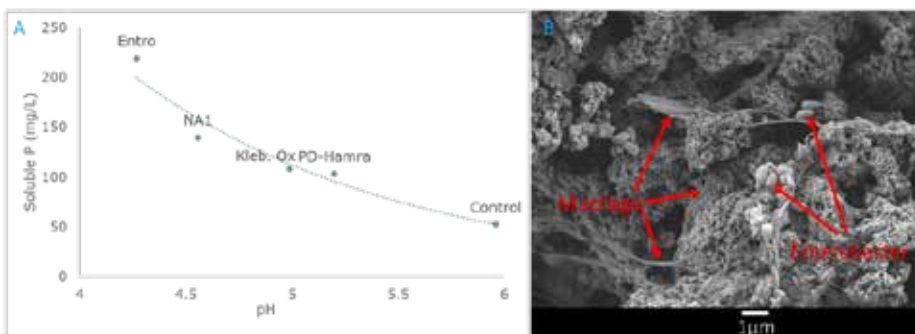


Figure 1: (A) P solubilization from apatite correlated with pH Reduction by different P solubilizing bacteria, including Enterobacter (Entro), and (B) SEM image of mucilage coated apatite with the presence of Enterobacter.

Calorimetric screening of microbial activity in a model condition of soil contamination

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Keywords: Bacteria; Ferriferous mineral phases; Contaminated soils; Isothermal microcalorimetry; Eco-dynamics.

Abstract

In this study, a calorimetry-based approach was applied to investigate the impact of Cd^{2+} , Pb^{2+} , and As^{3+} species on bacterial activity, depending on whether the heavy metals were present in an aqueous environment or substituted or adsorbed on an amorphous iron oxide [1].

For this purpose, power-time curves related to different stages of bacterial growth were recorded using a multi-channel microcalorimetric system TAM III equipped with nanocalorimeters operating under isothermal conditions at 298 K [2]. Additionally, the density of bacterial populations expressed as optical density was measured by spectrophotometry. Its correlation with the heat flow released at equivalent metal concentrations in aqueous solutions was established to quantify the rate of the exponential bacterial growth [3]. The half maximal inhibitory concentration (IC50) was determined to assess the eco-toxicity of the metal species. This approach was subsequently expanded to elucidate the toxicity of heavy metals present in doped ferrihydrite particles, serving as a model for iron oxide (Figure 1). The initial experimental findings with the aerobic strain, *Pseudomonas putida*, revealed that the IC50 parameter increased in the following sequence: $\text{Cd}^{2+} > \text{As}^{3+} > \text{Pb}^{2+}$.

These results are pivotal for advancing further investigations to unravel the impact of heavy metals on the growth and metabolism of both *Pseudomonas putida* and *Shewanella Putrefaciens*, while also considering various redox conditions between soil particles and these bacteria. Our ultimate goal is to comprehensively understand bacterial activity in soils contaminated with heavy metals.

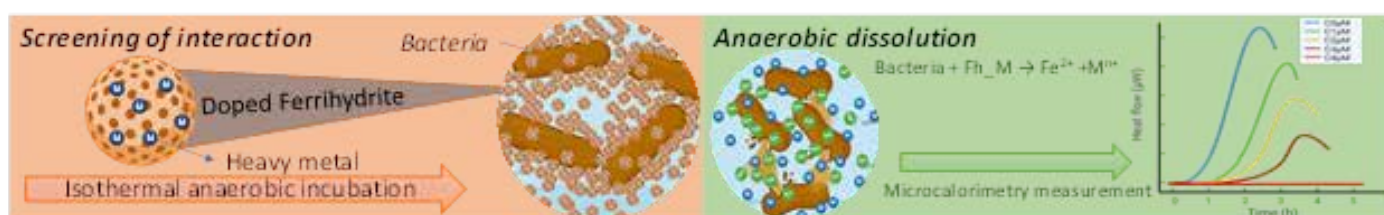


Figure 1: impact of doped heavy metals on Ferrihydrite on bacterial activity.

Acknowledgments

We would like to extend our sincere gratitude to the CNRS MITI Program for financial support and the technical staff of both research institutions for the assistance in implementing the appropriate experimental protocols. The authors also thank the Balard Platform Analysis and Characterization (UAR 2041 PAC Chimie Balard Montpellier) facilities for technical support.

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Quantifying the accuracy, uncertainty and sensitivity of soil geochemical multi-surface models

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Keywords: assemblage model; generic parameters; non-ideality; prediction interval.

Abstract

Geochemical multi-surface models and their generic parameters for the solid-solution partitioning and speciation of metals in soils have been used for decades to describe the availability and fate of heavy metals in the environment. Yet, the uncertainty and sensitivity of such models not been comprehensively evaluated.

We used statistical tools and a database of diverse soils from around the world to quantify for Cd, Cu and Zn the uncertainty for model parameters and input values of the multi-surface Non-Ideal Competitive Adsorption (NICA)-Donnan model for organic matter, coupled with the and Generalized Two-Layer Model (GTLM) for metal-oxides. Subsequently, we quantified the uncertainty of speciation predictions and the sensitivity to model parameters and input values.

Amongst others, this lead to new NICA-Donnan parameters that, especially for Zn, substantially improved model accuracy. Uncertainties generally followed Cu < Cd < Zn. With organic matter being the major binding surface across most soils, the humic acid affinity parameters (logK_i and n_i) were found to be most influential. Compared to a local “best-case” scenario where all relevant soil properties were measured, a global “simplified” scenario showed that assumptions about organic matter fractionation and metal-oxide specific surface area can be employed with a negligible reduction of model accuracy and only a small impact on model uncertainty.

Our results facilitate further adoption and well-informed parameterization of mechanistic multi-surface models by providing quantitative measures of prediction uncertainty and sensitivity. This is essential for the employment of such models in addressing societal challenges, such as the development and implementation of environmental protection criteria.

Metals and metalloids uptake and translocation in *Phragmites australis* specimens

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Keywords: toxic metals; plant translocation processes; mercury.

Abstract

Metals and metalloids enter into the aquatic environment from both natural and antropogenic sources. It is important to quantificate these elements, in particular toxic metals and metalloids, because of their highly resistance to degradation, their accumulation in water and sediment and their effects in living organism. In order to understand the accumulation and translocation of metals and metalloids in aquatic plant species, in this work we focused on specimens of *Phragmites australis* (common reed), one of the most abundant macrophytes in the study sites selected for this work: Alviano Lake and Paglia River basin (central Italy). The Alviano Lake is part of "Oasi di Alviano", a protected nature area (WWF) wich hosts a great variety of ecosystem habitats and communities. Since previous work¹ has revealed high concentrations of mercury (Hg) in this area due to old Hg mining activities upstream of the study area (Mt. Amiata), it was decided to include the Paglia River basin in the study site; in fact, this river has its source in Mt. Amiata. Along a transect from the river source to the Alviano Lake (about 100 km) we quantified 31 trace elements by triple quadrupole ICP-MS in environmetal matrices (water and sediment) and in the organs of *P. australis* (roots, rhizomes, stem and leaves) with the aim of assessing its capacity for uptake, translocate and accumulate metals and metalloids. This study allowed to identified the preferential organ of accumulation of trace elements in macrophyte studied and to assess the spatial distribution of contaminants up to the source.



Sampling site: Oasi di Alviano

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Advanced nanoremediation processes for the effective removal of complex mixtures of persistent pollutants from groundwater

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Keywords: nanoremediation; environmental nanotechnology; groundwater remediation; persistent pollutants; nanoscale zerovalent iron.

Abstract

Groundwater contamination poses a pervasive threat to human health and ecosystems, necessitating effective remediation strategies. Zerovalent iron nanoparticles (nZVI) have emerged as a powerful solution, offering unprecedented opportunities for in situ aquifer cleanup. Their efficacy is attributed to their nanoscale size, which endows them with high reactivity toward contaminants and ability to be injected into the subsoil, thus enabling targeted source treatment and plume remediation. nZVI-based treatments allow for effective removal of various contaminants including chlorinated solvents, metal ions, PAH, PCBs, and pesticides. However, some widespread contaminants, such as 1,2-dichloroethane (1,2-DCA) and 1,2-dichloropropane (1,2-DCP), are known to be resistant to this treatment, thus posing significant challenges for remediation of aquifers contaminated with complex contaminant mixtures.

In this study, an innovative nZVI-based reactant, IronGel Plus (DeltaNova), was tested at laboratory scale for the treatment of groundwater contaminated with a complex mixture of persistent chlorinated solvents. IronGel Plus consists of a viscoelastic biopolymeric gel containing reactive nanoscale zero-valent iron particles ($d_{50} < 100$ nm), functionalized by addition of a food-grade metallic catalyst to enhance their reactivity and effectiveness against contaminants. Batch tests at the laboratory scale have been conducted to assess the treatability of groundwater using nZVI, both as-is and catalyzed. Degradation tests were performed on groundwater samples collected at a real contaminated site. The study area is affected by contamination of the groundwater by chlorinated organic compounds at concentrations of thousands of $\mu\text{g/L}$. The contamination includes both compounds treatable effectively with zerovalent iron, such as PCE, TCE, and PCM, and pollutants highly resistant to nZVI (e.g., 1,2-DCA and 1,2-DCP). The effectiveness of the tested reagents in reducing the target contaminants over time was evaluated by determining the degradation kinetics of different compounds in contact with the different reactive materials.

Results demonstrated the effectiveness of nZVI in removing most chlorinated organic compounds, except for 1,2-DCP and 1,2-DCA. Moreover, partial and temporary formation of dichloromethane was observed as a result of the degradation of PCM and TCM. In the presence of IronGel plus, complete removal of all chlorinated solvents, including those resistant to treatment with zero-valent iron, was instead observed. Importantly, unlike simple nZVI, no formation of other intermediates or by-products was observed.

The effectiveness of remediation using catalyzed nZVI will be further evaluated in an upcoming pilot test in the field.

Acknowledgments

This study was partially carried out within the Ministerial Decree no. 1062/2021 and received funding from the FSE REACT-EU - PON Ricerca e Innovazione 2014-2020.

Study of the removal of copper by sorption onto lignocellulosic materials

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Keywords: Cu removal; lignocellulosic sorbent; sugarcane bagasse; lignin; surface complexation.

Abstract

Research in removal of metals from aqueous systems by bio-sorbents has been conducted for many years. It has been shown that both raw and modified sugarcane bagasse, or lignin were effective adsorbents for metals ions with efficient recovery and regeneration performance. The objective of this work was to study the possible metal removal capacity by raw sugarcane bagasse (SCB), residue after mild alkaline extraction, lignin precipitated from the extract, and a commercial lignin product. In conclusion, sorption mechanisms of metal cation were assumed and quantified.

In a first approach, characteristics of sorbents such as acid-base potentiometric titration and surface charge were analyzed by pH titration; specific surface area, pore volume and pore size by water and N₂ sorption, scanning electron microscopy, Fourier-transform infrared spectroscopy, and Raman micro-spectroscopy. Batch experiments were performed for studying sorption kinetics and sorption isotherms in the initial range of 0.01 to 1.0 mM Cu concentration, with either 0.01 or 0.1 M NaNO₃ as background electrolyte Cu concentration was analysed by Inductively Coupled Plasma Optical Emission spectroscopy. Cu speciation was calculated with Vminteq.

The results showed that pH plays an important role in the Cu sorption capacity on all sorbents. At pH 6, where the Cu sorption was the highest, the sorption equilibrium of Cu was reached after 2 h for SCB and residue, whereas it took 3 days for the commercial lignin, and only 30 min for the SCB lignin. Kinetic experimental data were better fitted with the pseudo-second-order model than with the pseudo-first-order. In the Cu concentration-range, at pH 6, sorption isotherms showed a BET-type shape with a plateau in their first part ($[Cu] < 0.2$ mM) before increasing at the highest Cu concentration ($0.2 < [Cu] < 0.8$ mM). The maximums of sorption capacity were in the order: SCB lignin, commercial lignin, SCB, and residue, corresponding to 5.1, 1.2, 1.0, and 0.74 $\mu\text{mol m}^{-2}$, respectively. The impact of the ionic strength in a 3 to 6 pH-range on the Cu sorption was not so important with a slightly higher sorption capacity at 0.01 M NaNO₃ than at 0.1 M NaNO₃.

In this presentation, we will show how, from the set of sorption experiments and surface characterizations, both the surface complexation and surface precipitation models can be used to better understand the sorption behaviour of Cu on such bio-sorbents in the pH range tested.

Reimagining the process of environmental remediation: An inventive “Up-and-Down” adsorption technique for eliminating Pyrene from acidic wastewater

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Keywords: Water remediation; Adsorption; Hybrid Alginate beads.

Abstract

Polycyclic Aromatic Hydrocarbons (PAH) pose a risk to human health because they are highly toxic, carcinogenic, and mutagenic [1]. In the context of water remediation, hybrid biopolymers are green materials that can reduce the pollutants in environmental matrices [2]. This study aims to propose a new and revolutionary “up-and-down” wastewater treatment system based on the adsorption of contaminants from the bulk and their transport to the surface to promote future remediation processes. Pyrene was selected as a model pollutant for PAH, and hybrid alginate beads, such as thermally modified hematite montmorillonite alginate calcium carbonate beads (@H@MACBs), were prepared to investigate their use in water remediation. The synthesized beads were characterized using FT-IR and ion-TOF mass spectrometry techniques, and adsorption studies were performed to quantify the remediation process efficiency and investigate the adsorption processes. Approximately 50% of Pyrene was removed from the aqueous solution without stirring after 90 min of contact time. A double increase in Pyrene removal was observed when the classical hybrid alginate beads were compared with the new modified hybrid alginate beads. This study contributes to efforts to deploy innovative remediation strategies to reduce the environmental impact of the textile industry, which is a significant contributor to global manufacturing and pollution.

Acknowledgments

Funding for this work was provided by PIA.CE.RI. 2020-2022 Linea 3 of the University of Catania Starting Grant Project for the project Advanced up and down photocatalyst for Chemical applications (ALYCE)

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Mucin-based Solutions for Water Decontamination

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Keywords: Mucin; Bio-sorption; Bio-synthesis; Metal wastewater; Selectivity.

Abstract

Biomaterials have emerged in recent decades as an alternative set of materials that can be employed in various water treatments, avoiding the use of costly or toxic synthetic materials. One intriguing biomaterial that has not been utilized for environmental applications is mucin, a natural glycoprotein with accessible binding sites and selective affinity towards different substances (e.g., metal ions, pathogens, particles), allowing it to protect internal organs in various living creatures. Mucin also has reduction ability for several noble metals, forming nanoparticles (NPs). Mucin's effectiveness in removing contaminants (such as mercury ions) was evaluated through several tests, including adsorption kinetics, isotherms and ion competition (Figure 1A) under different environmental conditions. Various techniques, like X-ray photoelectron spectroscopy, UV-visible and X-ray diffraction analyses, helped us understand how mucin interacts with and attracts different pollutants, revealing the mechanisms of removal. In addition, to use mucin in a practical and green fashion, mucin was processed into solid forms, such as nanofibers (Figure 1B), and was also assessed in water decontamination tests, offering convenience and recyclability. In several cases the adsorbed contaminant, such as gold ions, could be reduced and recovered, then used in a secondary treatment to further eliminate organic pollutants (Figure 1C). Overall, our studies have shown that mucin, as a biomaterial, holds a significant potential for various water treatment processes, highlighting its exceptional natural abilities.

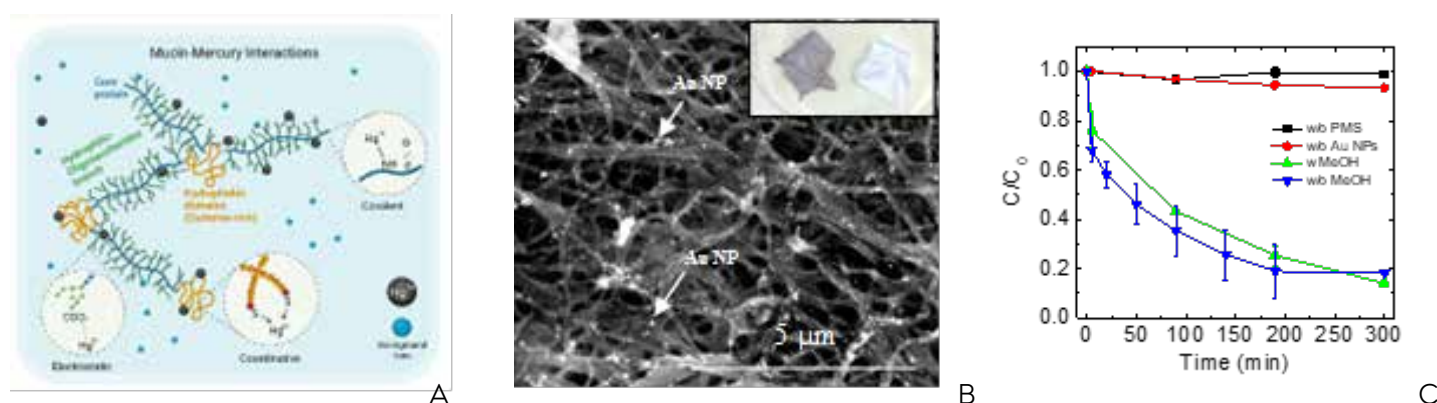


Figure 1: (A) Schematic illustration of suggested mechanisms for mercury removal using mucin. (B) Scanning electron microscope image of gold nanoparticles formed in a mixed-metal aqueous solution in the presence of mucin nanofibers (inset is an optical image of pristine nanofibers, right, and gold-embedded, left). (C) Removal of bisphenol A with mucin-recovered-gold nanoparticles in a peroxydisulfate activation.

Novel Biocompatible Trianglamine Networks for Efficient Iodine Capture

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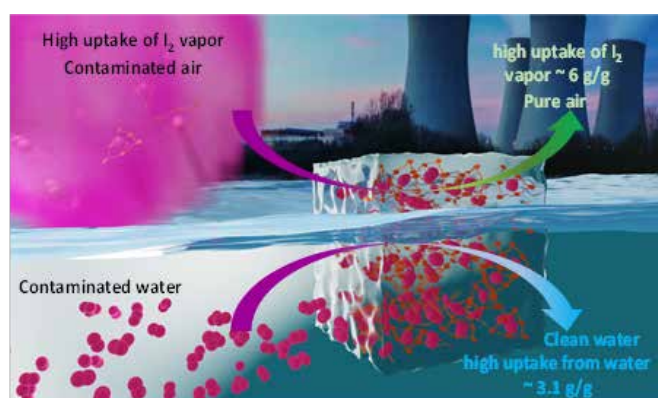
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Keywords: Macrocycle; Crosslinked Polymer; Iodine; Sorption.

Abstract

The International Energy Agency (IEA) predicts about \$1.1 trillion in investment in nuclear plants by 2040, representing a 46% increase in nuclear power generation worldwide. Due to this policy, it is urgent to come up with innovative solutions to prevent nuclear waste pollution risks. Nuclear waste substances, such as radioactive iodine produced from uranium fission, release volatile solid gases and can easily dissolve in water, posing serious threats to human population as well as the ecosystem. Radioiodine ¹³¹I and ¹²⁹I are the two main components of nuclear waste, with half-lives of 8.02 days and 15.7 million years, respectively. In this circumstance, it is vital to design smart materials able to capture radioactive iodine from vapor phase, water and seawater. The industrial technology to remove radioiodine from water is based on the chemical transformation of iodine into AgI using silver-doped adsorbents such as natural or synthetic zeolites. Or adsorbents such as silica-coated magnetite nanoparticles and hyperporous carbon. The limits of these sorbents are their low adsorption capacity, slow adsorption kinetics and inefficient recovery. Over the past years, new porous materials such as metal organic frameworks (MOFs), covalent organic frameworks (COFs) and porous organic polymers (POPs) shown high and fast adsorption capacity and good recyclability of iodine from vapor and aqueous phase. In our study, we report for the first time a biocompatible crosslinked trianglamine macrocycle network for the efficient iodine removal from vapor phase, water and seawater. In vapor phase, the crosslinked network could capture 6 g g⁻¹ of iodine, ranking among the most performant materials for iodine vapor capture. In liquid phase, this crosslinked network is also capable of capturing iodine at high rates from aqueous media (water and seawater). This network displayed fast adsorption kinetics and they are fully recyclable. This study reveals the high affinity of iodine with the intrinsic cavity of the trianglamine macrocycle. The synthesized material are extremely interesting since they are environmentally friendly, inexpensive and the synthesis could easily be scaled up to be used as the material of choice in response to accidents in nuclear industry¹.



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Purification of metal-polluted water by a lavandin-based hydrochar

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Keywords: hydrochar; adsorption; water depollution; heavy metals; surface complexation.

Abstract

Hydrochars are carbonaceous materials prepared by hydrothermal carbonization of biomass, with a number of applications ranging from energy production to catalysis and use as adsorbents for the decontamination of polluted water. In this work, hydrochars from waste of the perfumery industry (lavandin residues after hydrodistillation) have been chosen as the biomass source to obtain economical and ecological materials for the depollution of metal-polluted water.

Lavandin hydrochars were prepared at moderate temperature (180°C) and short retention time (4h), and were either used without any further surface modification or after treatment by sodium hydroxide or nitric acid.

Important chemical modifications were evidenced by characterization methods, in the number and nature of oxygen-rich functional surface groups such as carboxyl, lactone or phenolic hydroxyl functions.

The adsorption properties towards three divalent metals, nickel, lead and cadmium, have been studied both on single systems and ternary systems, with respectively, one metal or a mixture of the three metals interacting with the surface. The fast adsorption kinetics were well depicted by the pseudo-second order model, while the Langmuir model was used to interpret the isotherm data, showing a higher maximum adsorption capacity for lead (50 mg.g⁻¹) than for cadmium (17 mg.g⁻¹) and nickel (8 mg.g⁻¹). This higher affinity of lead for the surface was confirmed by a strong competitive effect, with a drastical decrease of the quantity of adsorbed cadmium and nickel in ternary systems, which was satisfactorily modeled using the extended Langmuir model. A surface complexation model was applied to interpret the data, with one single type of surface sites, both on chemically modified and unmodified hydrochars. The model showed a strong correlation between the number of carboxylate functions, depending on the chemical modification of the surface, and the adsorption properties. The surface complexation constants determined on single systems were successfully applied to account for the competition effects observed on the ternary systems.

Acknowledgments

S. S. Baran acknowledges Région Sud/Provence-Alpes-Côte d'Azur and the company Jyta in the name of G. Verger-Dubois for the financial support of her PhD fellowship, as well as Pôle innov'alliance. Pr P.-C. Maria is warmly acknowledged for providing lavandin samples.

Nitrogen enriched activated carbons for the CO₂ capture and separation

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Keywords: adsorption; CO₂ capture; activated carbons; CO₂ separation.

Abstract

Decarbonisation of industry is necessary to limit the impact of carbon dioxide gas emissions on global climate warming. Numerous researches are presently focused on the separation of carbon dioxide from industrial gases, the purification of biogas and also on the underground storage of CO₂. Adsorbent materials, in particular activated carbons, are promising for CO₂ adsorption or separation.

Activation of nitrogen-rich precursors with ammonia gas enabled to obtain various nitrogen-enriched activated carbons (nitrogen content up to 10 mass %). The starting materials are powdered chitosan (CS, 7 mass % N), freeze-dried chitosan hydrogel beads (BCS), coffee grounds (MC, 3 mass % N) and powdered polyacrylonitrile (PAN, 26 mass % N). Samples were prepared in two steps: (i) pyrolysis (10°C.min⁻¹, 900°C, N₂ 200 mL.min⁻¹) of pristine material and (ii) gasification at 900°C (NH₃ flow 20-40 mg.min⁻¹, contact time: 30-120 min) of the char obtained by pyrolysis.

The physisorption isotherms of N₂ at 77K and CO₂ at 273K indicate that the prepared activated carbons are mainly microporous (0.11-0.62 cm³.g⁻¹) with high ultramicroporous volumes (0.11-0.25 cm³.g⁻¹). Under similar activation conditions, the BET specific surface areas and microporous volumes of the activated carbons follow the trend: BCS > CS > MC > PAN. The initial porosity of the lyophilised beads promotes the activation and allows to obtain both microporous and mesoporous carbons (type I(b) + IV N₂ physisorption isotherm). The surface functionalities of some carbons were characterised by X-ray photoelectron spectroscopy (XPS) and elemental analysis (CHONS). The adsorption capacity of the studied activated carbons at 1 bar and 0°C tends to ~5 mmol.g⁻¹ as the BET specific surface area and the microporous volume increase. Higher CO₂ adsorption capacities were obtained for carbons from lyophilised chitosan beads (S_{BET}=1390 m².g⁻¹) and from chitosan powder (SBET=744 m².g⁻¹, 5.8 mass % N). The ideal CO₂ selectivities with respect to N₂ and CH₄ were calculated from the pure gases adsorption isotherms (0-35 bar, 0-75°C) for an activated carbon (CS, 60 min activation, S_{BET}=998 m².g⁻¹). The values at 1 bar are 21 and 3.4 for CO₂/N₂ mixture (15 vol. % CO₂, 50°C) and CO₂/CH₄ mixture (50 vol. % CO₂, 25°C), respectively, whereas the desired target selectivity is > 50 for the former.

Acknowledgments

National French Agency and France2030 for supporting the CATALPA ANR-22-PESP-0007 project from PEPR Spleen program.

Phytosterols and lipids for methane capture

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Keywords: Methane; Phytosterol; Nanoparticule; Capture; Henry's law.

Abstract

Methane (CH₄), a substantial driver of global climate change, is difficult to capture because of its low solubility in water (22.44 g.m⁻³ at room temperature and atmospheric pressure [1]).

In this study, various lipids were used in aqueous dispersions in order to improve this solubility, such as nanoparticles of rapeseed phytosterols, chemically modified phytosterols, olive oil and epoxidized soy oil. The chemical functionalization of phytosterols with glycerol carbonate in solvent-free conditions aimed to increase the ability of phytosterols to be dispersed in water. Water dispersions of phytosterols nanoparticles were produced by antisolvent precipitation with ethanol as the solvent and water as the antisolvent. We evaluated the influence of the nature, size and concentration of lipids dispersions on methane solubility in aqueous systems by following the apparent partition coefficient between gas and liquid phases defined by Henry's law.

The system composed of pure olive oil showed the best performance, with the lowest partition coefficient (7 kPa.m³.mol⁻¹ against 55 kPa.m³.mol⁻¹ for pure water) and the best selectivity for CH₄ against CO₂ (4.3 against 22.7 for pure water) (Fig. 1). Systems containing phytosterol nanoparticles also showed a lower partition coefficient, with 12.7 kPa.m³.mol⁻¹ for native phytosterols (5g/L in 50% ethanol). A selectivity of 6.3 was reached by the system containing raw phytosterol (16 g/L in pure water). Interestingly, systems with only 1g/L of amphiphilic phytosterol nanoparticles showed similar partition coefficient and selectivity to the system containing 20% of soy oil. These results show that nanoparticles of phytosterol improve methane solubility in aqueous medium by shifting the gas-liquid equilibrium of methane to the liquid part.

In conclusion, this work demonstrates that lipids such as phytosterol, dispersed in water at low concentration, are molecules of interest to participate in the remediation of CH₄ emissions and fight against greenhouse-effect gas.

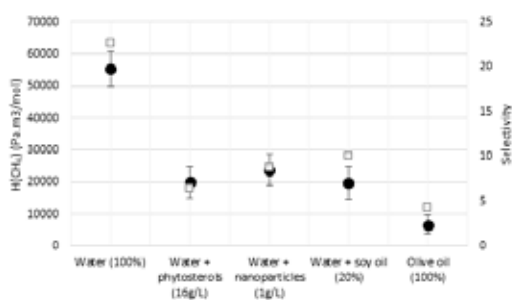


Fig. 1. Partition coefficient of CH₄ (●) and selectivity (□) with different absorbing phases. Selectivity was defined as H(CH₄)/H(CO₂)

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Composite graphene oxide multilayers for nanofiltration of cationic pharmaceuticals

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Keywords: wastewater treatment; composite membrane; graphene oxide; nanofiltration; anesthetics.

Abstract

Pharmaceutical products are released in wastewater streams from manufacturing sites and drug development bases. The production and use of a comprehensive portfolio of pharmaceutical products results in wastewater with a complex composition which is difficult to treat to levels in compliance with regulation from industry authorities. Nanofiltration (NF) have proved to be effective in the removal of various pharmaceuticals [1]. Three factors affect the efficiency of RO and NF in the removal of organic compounds (membrane, molecular, and background fluid characteristics) via three main mechanisms (size exclusion, interactions/adsorption, and electrostatic repulsion/attraction) [2]. Procaine is a local anaesthetic drug of the amino ester group. It is used primarily to reduce the pain of intramuscular injection of penicillin, and it is also used in dentistry. Today it is used therapeutically in some countries due to its sympatholytic, anti-inflammatory, perfusion-enhancing, and mood-enhancing effects [3]. Also, many compounds containing the acridine chromophore were synthesized and tested, and the aminoacridines bound wide use, both as antibacterial agents and as antimalarials, during World War II. With the current massive increases in drug-resistant bacterial infection, new acridine derivatives may be of use [4]. This study focuses on the removal of procaine and acriflavine using surface modified commercially available NF membranes, in a crossflow setup. Modification of the pristine membrane surface was performed by the layer-by-layer self-assembly of graphene oxide nanosheets and polymers, resulting in active multilayers of different thickness. The structure of the layer-by-layer self-assembled multilayers and the role of the layer number on the key membrane performance parameters will be discussed in details.

Acknowledgments

Project no. 126498 has been implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the KH funding scheme.

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Evaluation of porous carbon/CNTs Composite Membranes for Tannery Wastewater Treatment: Enhancing adsorption Efficiency through Membrane Filtration

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Keywords: Membrane filtration, Carbon nanotubes, Turbidity, Adsorption, Wastewater treatment.

Abstract

The complex discharge in wastewater laden with organic and mineral matter poses significant environmental and health risks. We appealed to address effluents from the textile and tannery industry through membrane treatment process by using carbon microfiltration membranes with an asymmetric structure. The macroporous support was prepared by extrusion following a previously optimized protocol in which graphite powder and phenolic resin were used as carbon precursors. The active microfiltration layer was deposited by slip casting of a suspension composed of an alcoholic solution of phenolic resin and ferrocene acting as carbon source and CNT growth catalyst agent, respectively. The membranes were characterized after heat treatment by scanning electron microscopy coupled to Energy Dispersive X-Ray analyses EDX for morphology and elemental analysis, while mercury porosimetry was employed to assess their porosity. The slip composition was optimized to yield a 120µm thick active layer with no apparent defect.

Two more materials consisting of a carbon/CNT and a carbon porous material labeled respectively as “graphitic-20/CNT” and “graphitic-0” were synthesized and tested for adsorption. Both materials were synthesized in solid cubic shape and then ground manually to obtain macrosized particles that were used for the tests. The adsorption behavior was evaluated through the treatment of a real sample of tannery wastewater pretreated using electrocoagulation process. The results revealed that both graphitic composites (graphitic-0 and graphitic-20/CNT) exhibited significantly enhanced adsorption performance. It turned out that the presence of the CNTs enhanced drastically the adsorption performance in the removal of turbidity, colour, conductivity and salinity. Moreover, this study underscores the effectiveness of these new carbon/CNT microfiltration membranes coupled with the adsorbents made of the same material for the treatment of tannery wastewater. Through rigorous analysis, the feasibility and efficiency of membrane filtration coupled to adsorption using this new carbon/CNT material for treating tannery effluent are brought to light.

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Heterogeneous Fenton Processes for Water Treatment

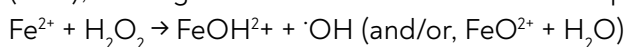
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Abstract

The classic Fenton reaction involves Fe(II) salts and H₂O₂ to produce reactive species such as the hydroxyl radical ($\cdot\text{OH}$), although other less reactive transients are probably formed as well (e.g. ferryl, FeO²⁺) [1]:



The radical $\cdot\text{OH}$ (and FeO²⁺ to a lesser extent) can react with contaminants and degrade them, for which reason the Fenton reaction can be used for water and wastewater treatment. The main disadvantage of the traditional Fenton process is the fact that it is most effective at pH 3, where recycling of FeOH²⁺ into Fe²⁺ and the $\cdot\text{OH}/\text{FeO}^{2+}$ ratio are most favourable. This issue entails the need to acidify water before treatment and correct pH after treatment, with eventual precipitation of Fe(III) sludge. For this reason, solid Fe-containing materials have been studied as an attempt to avoid sludge formation and extend the pH range towards less acidic conditions [2]. Magnetic materials are very interesting due to ease of separation from treated water, and zero-valent iron (ZVI) has shown considerable advantages over, for instance, magnetites because of much higher stability and ease of storage [3,4]. Compared with the use of ZVI as a reductant in groundwater remediation, the ZVI-Fenton process requires 1/100 to 1/1000 of the ZVI dose (mg/L vs. g/L) and, correspondingly, a fraction of the cost [5,6]. The pH range can be reasonably extended up to 5-6, in which conditions the ZVI-H₂O₂ technique can achieve complete degradation of contaminants of emerging concern (antibiotics, non-steroidal anti-inflammatory drugs, pesticides) and also affect potentially pathogenic bacteria, although it does not obtain anything near complete disinfection [7]. The overall reagent cost of ZVI-H₂O₂ would be around 0.04-0.07 USD m⁻³ [6].

Persulphate, peroxymonosulphate, sulphite, and metabisulphite have all been tested as potential alternatives to H₂O₂. Persulphate and peroxymonosulphate tend to produce a significant amount of SO₄⁻ that is more selective than $\cdot\text{OH}$, and about as reactive [8]. Sulphite and metabisulphite, with the latter used as cheap and stable sulphite source (it is also less dangerous than concentrated H₂O₂ to store and handle) produce a range of reactive species in succession: SO₃⁻, SO₅⁻, SO₄⁻, and $\cdot\text{OH}$. Excluding poorly reactive SO₃⁻, the role of the other transients depends on the degraded substrate: phenol will already react with SO₅⁻, while ibuprofen will require $\cdot\text{OH}$ for degradation [9].

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Optimization of the photocatalytic properties of g-C₃N₄ for environmental applications

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Keywords: heterogeneous photocatalysis; metal free semiconductors; green chemistry; chemometrics; graphitic carbon nitride.

Abstract

Graphitic carbon nitride (g-CN) is a metal-free semiconductor gaining interest within the scientific community for its simple preparation, low cost, and photo-electrochemical properties.¹ Noteworthy, there is no clear consensus on its optimal synthesis due to the several parameters affecting it.² In views of standardizing the synthesis of this heterogeneous photocatalysts and optimize its properties for environmental applications, in this work, we have calcinated melamine at different temperatures within the range 350 – 650 °C under anoxic controlled atmosphere and in presence and absence of an aluminium cover to reduce or enhance melamine sublimation, respectively. Obtained materials were characterised by several techniques, and their photocatalytic performance evaluated as H₂O₂ generation and phenol oxidative degradation under UVA and visible light, respectively. Results indicated that under UVA light, the best performance was obtained with the g-CN prepared at 425°C with the aluminium cover, leading to 6 mM production of H₂O₂ in 3 h, as well as a 3.4×10⁻² min⁻¹ phenol oxidation rate with an initial concentration of 100µM. To correlate the obtained data (21 variables analysed for 10 types of g-CN) a PCA was carried out, indicating that to maximize the photocatalytic performance under UVA light irradiation, employed temperatures should not exceed the 500 °C, contrarily to what is currently reported. On the contrary, for visible light experiments, reduction of band gap by doping the g-CN with nitrogen (employing higher temperatures, thus, observing a higher polymerisation degree and a C:N ratio close to stoichiometric 3/4 value) is required as usually observed in other works.

This work intends to shed light into the basic properties of g-CN and into the correlation between its photocatalytic properties and its physico-chemical features, as well as to promote the use of UVA light in views of saving synthesis costs of this semiconductor.

Acknowledgments

Project no. 126498 has been implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the KH funding scheme.

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Performance evaluation and optimization of a suspension-type reactor for use in heterogeneous catalytic ozonation

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Keywords: Catalytic ozonation; ozonation reactor; layered double hydroxides; particle rheology; organic removal.

Abstract

Packed fixed-bed reactors are traditionally used for heterogeneous catalytic ozonation. However, a high solid-to-liquid requirement, poor ozone dissolution, ineffective utilization of catalyst surface area, and production of large amounts of catalyst waste impede application of such reactors. In this study, we designed a suspension catalytic ozonation reactor and compared the performance of this reactor with that of a traditional fixed-bed catalytic ozonation reactor employing oxalic acid (OA) as the target contaminant [1]. Our results showed that total O_3 dissolved into the suspension reactor ($117\text{--}134\text{ mg}\cdot\text{L}^{-1}$) was much higher compared to that measured in the fixed-bed reactor ($53\text{ mg}\cdot\text{L}^{-1}$) due to a higher $O_3(\text{g})$ interphase transfer rate in the suspension reactor. In accordance with the higher $O_3(\text{g})$ interphase transfer, we observed a much higher proportional OA removal (32%) compared to that achieved in the fixed-bed reactor (10%) employing an Fe-oxide catalyst supported on Al_2O_3 ($\text{Fe-oxide@Al}_2\text{O}_3$) in both reactors. Use of a double-layered Cu-Al hydroxide (Cu-Al LDHs) catalyst [2] in the suspension reactor further enhanced the performance with nearly 90% OA removal observed. Given the superior performance of the suspension reactor, we investigated the impact of operating conditions (catalyst dosage, hydraulic retention time and ozone dosage) employing Cu-Al LDHs as the catalyst. We also developed a mathematical kinetic model to describe the performance of the suspension reactor and, through use of the kinetic model, showed that $O_3(\text{g})$ interphase transfer rate was the rate limiting step in OA removal. Thus, improvement in ozone gas diffuser design is required to improve the performance of the suspension reactor. Overall, the present study demonstrated that suspension reactors were more effective than fixed-bed reactors for oxidation of surface-active organic compounds such as OA due to the higher ozone interphase mass transfer rate and effective utilization of the catalyst surface area that can be achieved. As such, further research on suspension reactor design and development of catalysts suitable for use in suspension reactors should facilitate large-scale application of catalytic ozonation processes by the wastewater treatment industry.

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Chitosan-based reactive surface for disinfection and contaminants degradation

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Keywords: AOP; chitosan; heterogeneous catalysis; homogeneous catalysis; ferryl; contaminants of emerging concern.

Abstract

Chitosan is a very abundant and accessible biopolymer and in the last decades it was recognized as a promising material for several purification processes.

Because of its hydrophilicity, biocompatibility, its ability to form stable films, ease of modification, and remarkable affinity to metals, chitosan-based materials have become a promising candidate for several applications. We present a study aimed at the development of a chitosan-based separation film with surface catalytic properties, thanks to the presence of chitosan-metal complexes that mediate the oxidation of organic pollutants. Specifically, chitosan is proposed in place of an organic ligand creating a new organometallic catalytic membrane for water treatment. The initial part of the study focused on the development of a homogeneous chitosan-metal complex. The stoichiometry of the complexes was analyzed and their structures defined through molecular mechanics calculations. The catalytic efficiency of different complexes toward the homogeneous oxidation allowed to gain knowledge of the potential systems. The specific complex between chitosan and iron(III) was found to be the best organometallic system to be used as catalyst in the homogeneous oxidative degradation of water contaminants. This new catalyst was also fully investigated by combining experimental data with a kinetic model and DFT calculations of its most probable molecular structures. Once the homogeneous catalyst was created, a film of the complex chitosan-iron(III) was obtained and optimized in terms of stability in water and permeability, allowing the film to work as a catalytic surface. Moreover, its efficiency toward contaminant degradation as a heterogeneous catalyst provided promising results. The pure chitosan surface and the functionalized one, was tested as also as disinfectants presenting incredibly encouraging results.

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Fe-chitosan complexes for oxidative degradation of emerging contaminants in water: Structure, activity, and reaction mechanism.

Journal of Hazardous Material, 2021, 408, 124662-124671. doi.org/10.1016/j.jhazmat.2020.124662.

Adsorption-based water desalination: A bench scale performance evaluation

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Keywords: Physisorption; Desalination; Water purification; Bench scale tests; Mathematical modeling.

Abstract

Adsorbent materials may serve as a critical interface in combating pollution and contaminants in water treatment processes. By employing adsorption-based desalination technology, which relies on those materials, the removal of salt and organic compounds from saline and/or contaminated water sources can be achieved using low-grade heat. The technology investigated here operates through a phase change process occurring under vacuum conditions, involving the evaporation of saltwater and adsorption of water vapor onto an adsorbent material, leading to a heat-releasing phase, followed by the subsequent desorption and condensation of fresh water, thus achieving the regeneration of the adsorbent material [1,2]. This ongoing research focuses on optimizing the performance of adsorbent materials within this context, ranging from commonly available commercial options to novel in-house developed materials. Research activities are conducted using a bench-scale plant equipped to handle small quantities of adsorbent material (approximately 1 kg). Through systematic testing with different adsorbents and varying operational parameters, the aim is to identify the most efficient material for each specific condition. The work introduces the bench-scale plant, elucidates its operational principles, and underscores the validity of results to larger-scale implementations. The approach involves conducting adsorption cycles and empirically determining key performance parameters commonly employed in adsorption-based desalination plants. These performance parameters are then validated against data from other plants documented in existing literature. Concurrently, a lumped-parameter mathematical model of the system is developed to facilitate comparison between experimental findings and theoretical predictions of system behavior.

The results indicate that the performance parameters obtained are consistent with those reported in the literature for similar plants, implying the general validity of the findings found in this bench-scale plant. Consequently, this plant serves as a suitable platform for assessing the performance of different adsorbent materials across varied operating conditions, contributing to the ongoing research on this newly developed technology.

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Designing a Nature-inspired Engineering Tool to Address Soil Pollution

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Keywords: flocculation, permeability, CVOC, dechlorination.

Abstract

Chlorinated volatile organic compounds (CVOCs) form one of the most wide-spread forms of soil pollution on our planet; on industrial sites they can present as dense non-aqueous phase liquids (DNAPLs) and spread in the soil and groundwater. Therefore, we propose to build a vertical flow barrier in polluted soils by injecting metal – dissolved organic matter (DOM) flocs that will isolate the source zone and limit the spread. These flocs will also react with the contaminants to stimulate their microbial degradation through a dechlorination process, and remediate the soil pollution on the long term.

Aluminium (Al) and Iron (Fe) – which serve as coagulants to cover the surface of the DOM in the precipitation process – react differently when the pH and the metal to DOM ratio are altered. As a result, the flocs degrade more or less well, and can be used as an electron donor to enable the dechlorination of the CVOCs.

Use of biochar to remediate two different soils polluted by Pb and As

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Keywords: urban soil; biochar; lead; arsenic.

Abstract

Lead (Pb) and arsenic (As) are two metal(lloid)s that, among the numerous soil pollutants, tend to accumulate in both urban and agricultural soils. In New York City (NYC), this type of pollution accelerated since the industrial revolution and unfortunately persists in topsoil until today. Recent studies have shown that biochar presents an interesting potential as a sustainable material for soil remediation due to its physicochemical characteristics, such as the porous structure which allows a greater absorption of pollutants in soil (Qiu et al., 2022). In the two soils used for this reaserch, pollution is mainly due to lead arsenate, historically used as a pesticide in controlling common insect pests (*Lymantria dispar* L.) (Hood, 2006). One of the soils were from an urban garden in NYC, while the other from a suburban farm in New Jersey (Paltseva et al., 2018; 2020). The aim of this research is to examine the effect of biochar on the mobility of Pb and As in soils. Pot experiments are conducted in the greenhouse. Two different species of plants are used: *Brassica oleracea* var. *acephala*, common name: Lacinato kale, and *Brassica juncea* L., common name: Brown mustard. Six different treatments of soil were prepared (original soil; soil+1%biochar; soil+1%compost; Soil+1%biochar+1%compost; soil+2% biochar; soil+2% compost) as well as a garden soil serving as control. Each soil has five replicates, totaling 130 pots. Soil characterizations are performed before planting and after harvesting, and include texture, pH, salts, organic content, water holding capacity, nutrient contents, bioaccessible Pb and As, total elements using portable X-ray fluorescence (pXRF) and SEM-EDS. Morphological analysis of plants after growth will be carried out. It is expected that biochar will help stabilize Pb and As in soils by reducing phytoavailable metals and thereby plant uptake, as well as bioaccessibility of Pb and As.

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Revolving Algae Biofilm: An emerging green technology for wastewater treatment and biomass production

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Keywords: algae-based technology; revolving algae biofilm; wastewater treatment; nutrient recovery; biomass production.

Abstract

Towards the direction of zero-carbon emission and green technologies for wastewater treatment, algae-based technologies are considered promising candidates to deal with the current situation of pollution and climate change. Recent developments of algae-based technologies have been introduced in previous studies in which their performances were optimized for wastewater treatment and biomass production. Conventional algae-based technologies include photo-bioreactor, airlift reactor, flat panel airlift reactor, high-rate algae pond, and rotating disks reactor. The limitations of these technologies focus on biomass yield and harvesting. Therefore, revolving algae biofilm reactor (RAB) has been researched and developed to overcome these disadvantages. The RAB has been proven to have great potential in high biomass productivity, simple harvesting method, great CO₂ capture, high light-use efficiency, and good nutrient uptake. However, there were few articles detailing RAB performance, which concealed its enormous potential and diminished interest in the model. Hence, this review aims to reveal the major benefit of RAB reactors in simultaneous wastewater treatment and biomass cultivation. However, there is still a lack of research on aspects to upgrade this technology which requires further investigations to improve performance or fulfill the concept of circular economy. By shedding light on the nuanced interplay between hydraulic retention time, biomass retention time, salinity, microalgae - bacteria ratio, C/N ratio and nutrient removal, biomass growth, these studies will contribute valuable insights that can inform the practical application and optimization of revolving algae biofilm reactors in wastewater treatment. This underscores the substantial potential of the RAB, laying a robust foundation for practical applications in the future.

Activated carbons with supported magnetic particles for the removal of micropollutants from wastewater

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Keywords: activated carbons; micropollutants; adsorption; water remediation.

Abstract

Many micropollutants (pesticides and their metabolites, pharmaceuticals, per- and polyfluoroalkyl substances (PFAS)) remain present in water at the outlet of wastewater treatment plants and even in drinking water, hence the interest in developing materials capable of adsorbing them at very low concentrations.

In this context, activated carbons were synthesised by gelification in a basic medium (NaOH) of droplets of acid solutions of chitosan containing Fe₃O₄ nanoparticles, followed by a thermal activation (700-900°C). This method allows the formation of millimetre-sized adsorbent beads having a multiporous scale (micro, meso, macro) and BET specific surface areas (N₂, 77K) of 200 to 780 m².g⁻¹. Some of these beads have magnetic properties that make them easy to separate from the aquatic environment.

The adsorption kinetics of beads and powders resulting from their grinding were studied for a mixture of six contaminants dissolved in a mineral water (pH 7.3, 25°C, 0.1 g.L⁻¹): bisphenol A (BPA), carbofuran (CBF), carbamazepine (CBZ), diclofenac (DCF), dimethoate (DMA) and imidacloprid (ICP). The concentrations of the contaminants were measured by LC-MS/MS.

While the adsorption kinetics on the beads are slow (equilibrium time ~ 24 h), the powdered samples seem to be more efficient: for an initial concentration of 50 µg.L⁻¹ of each pollutant (0.1 g.L⁻¹ of adsorbent), 50 to 99% of the micropollutants introduced into the solution were removed after 4 h of contact time.

The adsorption isotherms, studied for an activated carbon powder containing Fe₃O₄ (pH 7.3, 25°C, 24 h, 0.2-40 µg.L⁻¹) are of Langmuir type (CBF, CBZ, DCF) or follow Henry's law (BPA, DMA, ICP). The adsorption capacities are about 4 times higher for bisphenol A and carbamazepine, in relation to the high polarisability of these molecules. Although diclofenac has the highest polarisability, its negative charge induces a repulsion with the negatively charged activated carbon surface at the working pH (pH_{pZC} ~ 4).

The degradation of the micropollutants was tested in the presence of peroxodisulfate ions (S₂O₈²⁻) for a solution containing the six micropollutants in which an activated carbon/Fe₃O₄ adsorbent was dispersed. Within the first few minutes of contact time, a significant reduction in concentration of all the micropollutants was observed. Complete degradation was observed after 10 minutes, thanks to the catalytic effect of the Fe₃O₄ supported particles.

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The authors thank Campus France for the grant provided to Niravkumar P. Raval (MOPGA-4 programme).

Electromigration to remove phosphate ions from an aquaculture pond by adsorption

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Keywords: electromigration; phosphate pollution; zeolite; adsorption; laboratory scale pond.

Abstract

Water pollution by phosphates is an environmental problem as it promotes eutrophication, leading to oxygen depletion and ultimately species extinction. In Vietnam, many aquaculture farms practice intensive shrimp farming for local and international consumption. Analysis of farm water quality showed that phosphates levels were difficult to control and increased over time, due to their contribution (i) from shrimp feed and (ii) from waste produced by the shrimp themselves.

The aim of this work is to study an alternative, ecological and economical treatment approach capable of containing chemical pollution in a shrimp farming pond. To achieve this, a laboratory scale pond has been built. A local zeolite from Vietnam was used as natural adsorbant and placed between two membrane filters on each side of the small-scale pond (Fig.1). Two graphite electrodes were placed on each extremity of the pond and an electric field was applied to these electrodes via a voltage generator in order to provoke phosphate migration towards the cathodic compartment. Phosphate ions were immobilised by adsorption on the surface of the zeolite when entering in contact with it. The concentration of phosphate ions in the anodic and cathodic compartments of the pond were monitored in order to determine the immobilization efficiency by the zeolite, and the duration of treatment efficiency (estimation of the time required for phosphate to pass through the cathodic compartment). The physico-chemical parameters monitored during the experiment were conductivity, pH, phosphate concentration. Batch adsorption experiments were carried out and thermodynamic models were used to determine the nature of the physico-chemical interactions and the ion trapping efficiency of the zeolite. Electrokinetic laws were used to attempt to model the phosphate migration in water and through zeolite.

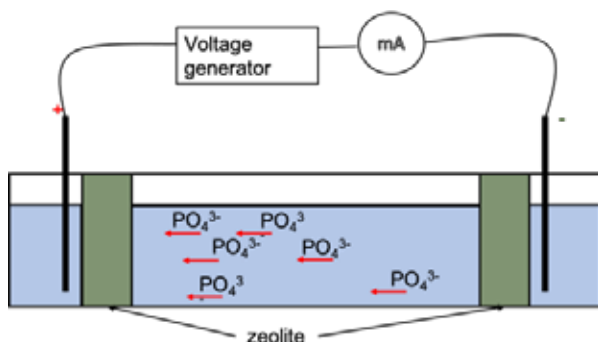


Fig. 1: Schematic representation of the laboratory scale pond (x1/200)

Acknowledgments

This work was supported by the French government through the France 2030 investment plan managed by the National Research Agency (ANR), as part of the Initiative of Excellence Université Côte d'Azur under reference number ANR15-IDEX-01.

Modelling flocculation

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Keywords: flocculation; clay; organic matter; Population Balance Equations; Logistic Growth

Abstract

Flocculation, the aggregation between different particles to form a large cluster (floc), is a phenomenon that is key to understand the transport of clay and organic matter as well as nutrients and contaminants in water. Traditionally, the growth of flocs is modelled using so-called Population Balance Equations (PBE) models [1]. Unfortunately, such models rely on hypotheses that are questionable and parameters that cannot be quantified experimentally. Another disadvantage is that PBE models are CPU intensive and therefore not fit to be integrated in large-scale transport models.

We opted for a different approach, whereby we developed a logistic growth (LG) model that is easy to implement and not CPU demanding [2]. This model was conceived by studying both data from literature and data collected by us [3,4]. It was found that the time evolution of floc sizes and numbers of particles of a specific size could be correctly modelled using the LG model [5]. The LG model also captures correctly the kinetics of flocculation, whereas the PBE model does not [5]. The model parameters dependence on important factors, such as clay and organic matter concentration, salinity and shear rate was studied in the lab, and enabled to parameterize the LG model [5-7].

The parameterized LG model is implemented in Delft3D, a large-scale sediment transport model that is used to estimate sediment fluxes in coastal (port) areas. The model will be tested using in situ measurements that determine clay concentrations and particles sizes, following the protocol described in [2]. One important next step will be to include erosion/deposition mechanisms in the model. We are currently working on studying the large strain consolidation of flocculated/non-flocculated sediment.



Flocs recorded close to the coast, near Rotterdam (size $\pm 100 \mu\text{m}$)

Acknowledgments

Deltares is gratefully acknowledged for the use of the laboratory equipment.

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Conditional existence of Donnan potential in soft particles and surfaces: dependence on steric effects mediated by electrolyte ions and structural charges

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Keywords: Soft particles/interfaces; Electrostatics; Donnan potential; Steric effects; Modified Poisson-Boltzmann theory.

Abstract

The Donnan partitioning of ions at charged surfaces and permselective interfaces has major implications e.g. in biology, as it affects the permeability of the membrane of bacteria to nutrients or antibiotics, it contributes to bacterial survival under adverse (osmotic) environments and it connects to biological functions like electric signalling in nervous system.

According to the classical Poisson-Boltzmann theory for soft interfaces [1], a Donnan phase is established in a polyelectrolyte layer at sufficiently high salt concentrations when the condition of a thin electric double layer (EDL) relative to the soft layer thickness is fulfilled. Since then, corrected Poisson Boltzmann models have been proposed to account for ion-size (steric) effects. Although the significance of the latter at sufficiently large electrolyte concentrations have been evidenced in literature [2], their implications on the Donnan regime features and interfacial Donnan partitioning of ions have received little attention. Accordingly, based on a recent modification of mean-field Poisson-Boltzmann theory for ion steric effects [3], we have developed a formalism that addresses both the existence and magnitude of the Donnan potential in soft layers as a function of key electrostatic descriptors of the soft interface (thickness, density and size of structural charges) while scrutinizing the impacts of molecular properties of the electrolyte including counterion/co-ion size and valence ratio and ionic strength [4]. The results derived demonstrate that the existence of a Donnan potential in a soft layer is conditioned not only to large values of the layer thickness compared to a here-defined Debye length operative within the shell, but to additional verification of a criterion that involves space charge density of the layer, solution ionic strength and a nondiluteness electrolyte parameter that depends on ion size and valence. In order to address the molecular mechanisms governing the screening power of the counterions in the soft layer, and therewith the magnitude of the Donnan potential (if established), our analytical and numerical results are systematically compared to predictions from Ohshima's theory on soft surface electrostatics [5] where ions and layer charges are assimilated to immaterial points. Overall, among the key results reported in this contribution is the demonstration that structural charge screening at a soft interface with consideration of finite ions volume can exceed the predictions of classical mean-field theory.

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Modelling trace metal binding to humic matter: presenting NICA-SPBT-PEST and discussing the validity of ‘generic’ parameters.

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Keywords: Humic matter; Trace metals; NICA; Poisson-Boltzmann, PEST.

Abstract

Natural organic matter, of which humic matter is a main component, plays a key role in the complexation, mobility and toxicity of trace metal ions in the environment. The description of trace metal binding to humic matter is currently carried out using either NICA (Non-Ideal competitive adsorption)-Donnan or WHAM modelling framework, despite of the recognized limits of these models with regard to their treatment of particle electrostatics [1]. The electrostatic and proton binding parameters are then generally obtained from the fitting of potentiometric titrations measured at different ionic strengths and the metal binding parameters are retrieved from the fitting of metal titrations collected at various pHs. As an alternative to NICA-Donnan or WHAM, we proposed recently an electrostatic model more rigorous than the NICA-Donnan representation with the formulation of a Soft Poisson-Boltzmann Theory (SPBT), and we applied it successfully for the quantitative description of proton binding to different types of particulate humic matter [2]. In that work, the electrostatic and chemical parameters were optimized to reproduce the proton titration data (charge vs. pH) and the corresponding affinity spectra at different salt concentrations [3].

In this contribution, we extend our previous work to consider the competition between metal ions and protons in their respective binding of organic matter by considering NICA isotherms in combination with SPBT electrostatic formalism (so-called NICA-SPBT model). The metal binding parameters were successfully optimized to correctly account for competitive metal titration data measured at different pH values for a total of twelve different metal titrations curves pertaining to copper, lead, cadmium, zinc and humic matter samples for which we derived the relevant electrostatic and proton binding parameters in our previous report [2]. The optimized metal parameters were obtained from the coupling of our home-made Fortran code for NICA-SPBT computations with PEST, an open-source software for parameter estimation [4]. Singular Value Decomposition (SVD) was adopted in PEST optimization environment to ensure parameter orthogonality and post-processing analyses of variance and uncertainty. For the sake of comparison, reported ‘generic’ NICA-Donnan parameters were further considered to simulate the metal titration curves of interest and they were systematically compared to the outcomes from optimised NICA-SPBT -based approach. It is found that the capability of the ‘generic’ NICA-Donnan parameters to describe the experimental results is generally poor, and the reasons for this failure are discussed in detail.

Acknowledgments

JFLD and JPP are grateful to national project Labex Ressources XXI for funding the post-doctoral scholarship of JW.

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Chromium(III) Binding to Purified Fulvic and Humic Acid and its Solid Solution Partitioning and Speciation in Soil .

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Keywords: Chromium; Organic matter; geochemical modelling; NICA-Donnan; binding parameters.

Abstract

Chromium (Cr) is a metal of high environmental concern due to its toxicity; its speciation is controlled by binding to organic matter (OM) when present as Cr(III), yet absence of accurate binding parameters makes its behaviour difficult to model. This study focuses on the derivation of improved Cr binding parameters for the OM binding model NICA-Donnan (ND). Adsorption experiments to humic- and fulvic acid were conducted using the Donnan membrane technique, distinguishing between free Cr and humic-bound Cr. ND parameters were subsequently derived to give an optimized description of the adsorbed Cr. This was done in multiple scenarios, considering solely free Cr^{3+} adsorption and in conjunction with adsorption of $\text{Cr}(\text{OH})^{2+}$ or $\text{Cr}_2(\text{OH})_2^{4+}$. New parameters were thereafter validated against various datasets.

The scenario considering Cr^{3+} and $\text{Cr}_2(\text{OH})_2^{4+}$ adsorption gave a most accurate description of experimental results (left figure). The new parameters have significantly lower affinities compared to the original “generic” parameters, which were derived based on linear free energy relationships [1]. Application of the new parameters in modelling Cr speciation in a contaminated soil results in an improved prediction of free Cr^{3+} (right figure), yet a worsed prediction of total dissolved Cr. pH dependent Cr leaching from solid waste is significantly better described when applying the new parameters. It can be concluded that the new parameters are a significant improvement over the original parameters, yet they underestimate Cr binding to OM. Overall they allow for a better description of Cr speciation in the environment, which aids in understanding the environmental risks associated with Cr pollution.

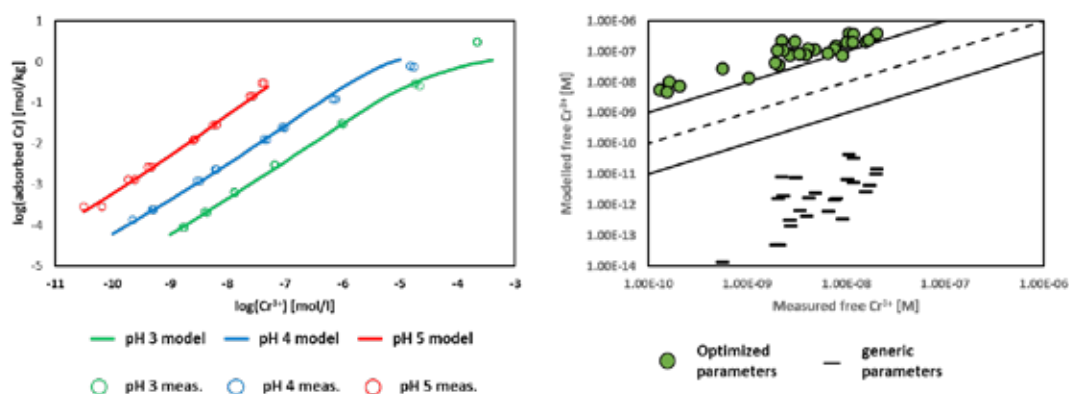


Figure 1: (left) Optimized fit of ND parameters for Cr binding to fulvic acid, considering adsorption of Cr^{3+} and $\text{Cr}_2(\text{OH})_2^{4+}$; (right) measured free Cr^{3+} concentrations in a contaminated soil against modelled concentrations using the generic parameters of Milne [1] (black hyphens) and as calculated using optimal parameters considering adsorption of Cr^{3+} and $\text{Cr}_2(\text{OH})_2^{4+}$ (circles).

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Does a Humic Model Disintegrate Upon Dilution? A Molecular Dynamics Simulation of Water Content Effects

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Keywords: humic substances; molecular dynamics; aggregate stability; dilution.

Abstract

Natural organic matter (NOM) and humic substances (HS) as its part are key players in diverse biogeochemical processes occurring at the interfaces in different scales, contributing to the carbon cycling, sorption reactions, transport and environmental fate of chemicals and biological activity. Hence, there is a continued interest in understanding the structure of NOM/HS and modeling their physico-chemical characteristics. Molecular simulations play an important part in this quest due to the possibility of performing machine experiments and verifying hypotheses raised regarding the structure of HS. This work intends to examine how stable HS could be upon the dilution in water, if they would be considered to represent aggregates formed by small molecules capable of electrostatic, H-bond and van-der-Waals interactions. In this way, one may probe the vision of HS as supramolecular structures formed of small molecules instead of representing relatively large molecular entities. The HS models were developed using Vienna Soil Organic Matter Modeller [1], for a sample resembling a C13 NMR-derived carbon type composition of the standard Leonardite humic acid (HA). The models were built by varying the molecular size, amount of water and the counter cation (sodium vs calcium), while keeping the chemical composition identical, to link low-hydrated HS systems with aqueous NOM solutions in the concentration range of environmental significance. Molecular dynamics simulations have been performed for 100 ns at constant temperature (300 K) and pressure (1 bar), thus allowing monitoring of the size and number of HS aggregates, and the concentrations of HS atoms in the vicinity of HS molecules and at different distances. The simulations demonstrated that HS aggregates disintegrate upon the dilution, the process occurring essentially more easily in the presence of monovalent sodium however taking place also with divalent calcium. An aggregating role of calcium in HS organization is found in agreement with earlier modeling of lower-hydrated HS systems [2]. The strong interactions within the HS aggregates remain at the level of dimers of small molecules revealing a high stability against dilution. Hence, the simulation results suggest that the aggregation of HS occurs in a step-wise mode rather than cooperatively, whereas the presence of sodium as a balancing counter ion is a strong disintegrating factor. Further implications linking the simulation results with the present experimental data on the apparent molecular size and mass of Leonardite HA are discussed hinting that the possibility of the existence of large-size HS molecules undergoing step-wise aggregation should be taken into account in considering HS properties in aqueous solutions.

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Application of standardized colloid mixing in terms of rate of coagulation to evaluate various types of flocculants in the early stages of flocculation

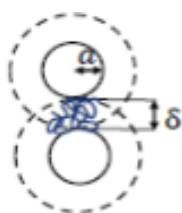
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Keywords: colloid mixing; rate of flocculation; polymer flocculant; polyion complex; clay.

Abstract



$$\frac{dN}{dt} \sim (a_0 + \delta)^3 ; \quad \beta = \frac{(a_0 + \delta)^3}{\alpha_T a_0^3}$$

$\delta \approx$ thickness of adsorbed polymer layer

$\alpha_T =$ capture efficiency

While analyzing the aggregation process of model colloids, we learned that the aggregation velocity is determined by the turbulence intensity. This proposition, taken in reverse, means that complex turbulent phenomena can be evaluated from the rate of aggregation if the aggregation rate of colloidal particles is limited by collision process. With this idea, turbulent mixing is normalized by the rate of rapid aggregation of model colloid particles and the method of normalized colloid mixing (NCM) was established. So far, NCM has been applied to many systems involved with polymer flocculants to elucidate the transient behavior polymer adsorption onto bare colloid particles. In the present study, the validity of NCM is revisited using flocculation induced with mono-dispersed colloidal spheres placing an emphasis of capture efficiency and enhancement factor of flocculation with polymer flocculants. In addition, application of NCM to different type of flocculants, i.e., poly ion complex, montmorillonite, modified lignin, and so on, were introduced to reveal out the formation of architecture of these flocculants on the surface of colloidal particles.

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Financial support of JSPS Kakenhi 22H00387 is acknowledged.

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Does It Slip? Water Flow at the Solid-Liquid Interface of Porous Media: Insights from Spectral Induced Polarization

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Abstract

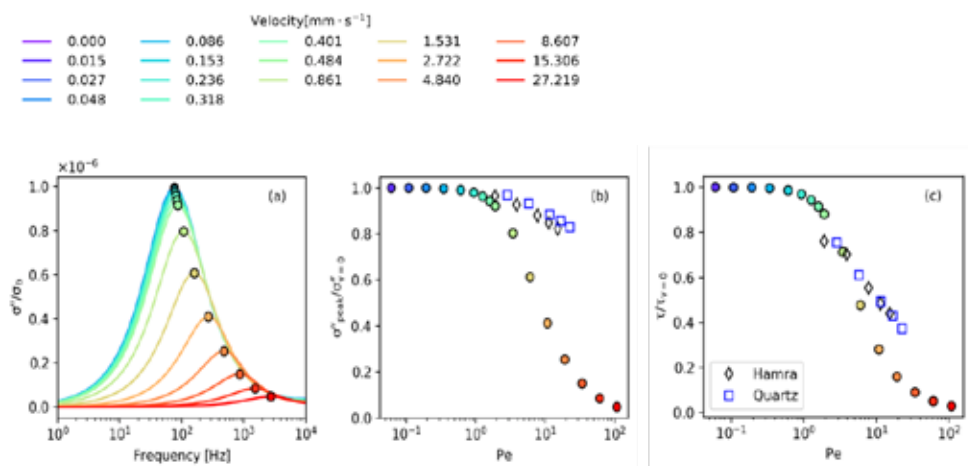


Figure 1. (a) Quadrature conductivity spectra from numerical simulations using slip boundary conditions at varying fluid velocities. Relative decrease in polarization magnitude (b) and relaxation time (c): comparison between synthetic and experimental data.

Previous studies and models of spectral induced polarization (SIP, aka impedance spectroscopy) have not considered the impact of water flow, assuming that the key contribution to SIP comes from Stern layer polarization where water is presumed stationary. This study investigates the effect of pore water velocity on SIP signature of porous media through experiments and modeling. We measured SIP response (0.1-100 Hz) of soil types under varying velocities, both ascending and descending. We extended the classical SIP model, based on Poisson-Nernst-Planck equations, by incorporating Stokes equations for water flow and exploring both slip and no-slip boundary conditions (BC). Our experimental results demonstrate that increasing water flow significantly decreased polarization magnitude (approximately 30%) and relaxation time (approximately 60%). These findings were consistent across soil types with no observed hysteresis. Numerical models with no-slip BC failed to reproduce experimental results, while models with slip BC qualitatively agreed with experiments but overestimated flow impacts, suggesting partial slip may be more realistic. Numerical analysis revealed that water flow deforms the electrical double layer (EDL), reducing its length and surface potential, explaining the observed decreases in polarization and relaxation time. These results demonstrate the sensitivity of SIP to fluid flow, emphasizing the importance of considering flow velocity in SIP data interpretation. This work opens new avenues for non-invasive characterization of fluid flow at the EDL scale, with potential applications in porous media studies, microfluidics, electrochemistry, fuel cell research, and more.

Acknowledgments

This research was supported by the Israel Science Foundation (grant No. 2488/22)

Structural-controlled formation of nano-particle hematite and their removal performance for heavy metal ions

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Keywords: iron oxide; hematite; nanoparticles; crystal growth; heavy metals; CD-MUSIC model.

Abstract

Hematite is ubiquitous in nature and holds great promise for a wide variety of application in many frontiers of environmental issues such as heavy metal remediation in environments. Over the past decades, numerous efforts have been made to control and tailor the crystal structures of hematite for improving its adsorption performance for heavy metal ions (HMIs). It is now well established that the adsorption behavior of hematite nanocrystals is strongly affected by their particle sizes, crystal facet contributions, and defective structures. This review overviewed the size- and facet-dependent hematite, as well as the defective hematite according to their fabrication methods and growth mechanisms. Furthermore, the adsorption performance of various hematite particles for HMIs were introduced and compared to clarify the structure-active relationships of hematite. We also overviewed the advances in charge distribution (CD)-multisite complexation (MUSIC) modeling studies about the HMIs adsorption at hematite-water interface and the binding parameters. Present review systematically describes how the formation conditions impact the structural and surface properties of hematite particles, which provide new strategies for improving the performance of hematite for environmental remediation.

Hematite has widely been accepted as an efficient adsorbent for HMIs, offering us the possibility of a simple and rapid approach for the removal of environmental contaminants. The study of hematite in the field of soil remediation, however, is currently in the preliminary stages, and further study needs to be conducted. A better understanding of in situ environment behaviors and the influence factors of HMIs adsorbed on hematite has also not been clearly demonstrated. It requires a range of laboratory and field testing to generate comprehensive data to confirm the application of hematite in environmental for in situ remediation.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 32061123007 and 41977023).

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Modelling Biogenic Manganese and Iron Oxide Generation and Subsequent Removal of Organic Micropollutants

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Keywords: Activated carbon; adsorption; manganese oxides; micropollutant degradation; modelling.

Abstract

The ability of both biological activated carbon (BAC) filters^{1–3} and Mn and Fe oxides^{4,5} (MFOs) to remove organic micropollutants (OMPs) from water is well-established, but their coupling and mechanisms of OMP removal still require elucidation. To that end, a new model describing the generation of biogenic MFOs and subsequent OMP oxidation and removal (Fig. 1) is devised and validated. It incorporates a) the diffusion and electro-migration of the metals and select OMPs through the biofilm and MFOs⁶; b) the chemical reactions governing biogenic MFO generation as well as OMP oxidation by MFOs⁷; and c) the adsorption process of OMPs on MFOs and on activated carbon granules⁵. Using data obtained from literature, the kinetics of the pertinent reactions are estimated, alongside the relevant mass transfer parameters and adsorption isotherms. In the future, this model will be expanded upon and can be integrated into a greater BAC model that would include all relevant OMP processes. This will enable the optimization of BAC filter performance and dynamic operation.

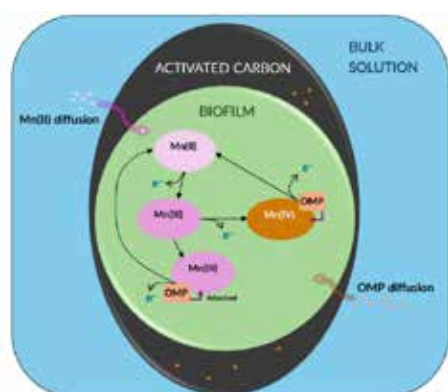


Figure 1: Schematic of the processes involved in the proposed model of biogenic Mn(IV) generation and subsequent OMP removal

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Early breakthrough of activated carbon filters for PFAS removal: mechanisms and technology development

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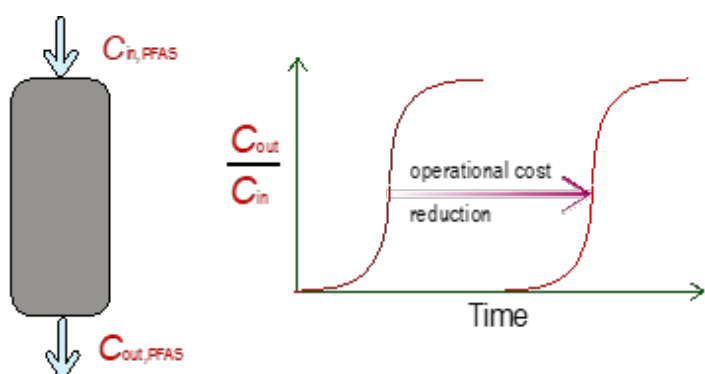
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Keywords: PFAS; adsorption; activated carbon columns; regeneration.

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a class of halogenated hydrocarbons known for their unique properties, making their removal in water treatment a significant challenge. Drinking water companies that use surface water for their production process, face challenges meeting the stringent guidelines set by the European Union. Adsorption is a commonly applied technology in water treatment, but frequent regeneration is required, resulting in high operational costs. In this presentation, we will discuss the effect of the initial concentration on the adsorption equilibrium, for several different types of PFAS, and at different concentration ranges. We will discuss, in a quantitative manner, the mechanisms resulting in a fast breakthrough of PFAS in activated carbon filters. The effect of different types of PFAS will be quantified, including short-chain and long-chain, with different surface groups. A theoretical model will be presented describing adsorption of PFAS on the activated carbon surface, transport of PFAS in the activated carbon granules and transport of the solution (water) and the solvents (PFAS) in the activated carbon column. This model is validated with experimental data and thereafter used to determine the factors resulting in rapid breakthrough.

Graphical abstract:



Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a class of halogenated hydrocarbons, including, amongst others, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). These substances are used, because of their special properties, in the production of Teflon, and are applied in fire-fighting foam. In the past years, increasing concentrations of PFAS have been detected in the environment, and these chemicals are suspected to cause adverse effects on human health and on the environment.

PFAS have very special properties. Firstly, they have a non-polar hydrophobic carbon chain structure, attached to a hydrophilic polar functional group. Therefore, these components are amphiphilic, and they can associate both with water and oil. Secondly, these compounds are very stable and resistant to biodegradation. The combination of these properties makes that these compounds are of concern in water treatment, as removal (for example by adsorption) and (bio)degradation are both challenging.

Drinking water companies that use surface water for their production process, detect PFAS in their source water. In recent drinking water guidelines by the European Union, the maximum concentration of PFAS has been set to 0.5 µg/L, and a recent EU proposal suggests a stricter limit of 4.4 ng/L (Proposal for EU directive, 2022). Especially drinking water companies that use surface water as their primary source will not meet this stringent guideline set by the EU, mainly because of upstream industrial discharges. Therefore, there is an increasing need for treatment technologies to remove PFAS during drinking water treatment.

Several drinking water treatment technologies for the removal of PFAS are available, including the application reverse osmosis (RO), powdered activated carbon (PAC) or granular activated carbon (GAC). Reverse Osmosis can potentially be used, but this would produce a large concentrate stream with PFAS at concentrations requiring treatment before disposal. The application of PAC would result in large amounts of sludge, which must be treated. The application of GAC, however, would require frequent GAC regeneration. Although adsorption is an effective technology in reducing PFAS levels in drinking water, rapid breakthrough of PFAS is often observed, which requires frequent adsorbent regeneration, increasing treatment costs (Belkouteb et al., 2020).

In recent adsorption experiments, we found that, with GAC, adsorption of PFAS on activated carbon was very limited, see Figure 1. Batch bottle experiments were performed, and at low initial concentrations, the adsorption capacity on activated carbon was in the range of 10-30 ng/mg, depending on the type of PFAS. In scientific literature, much higher adsorption capacities have been reported at much higher concentrations in the bulk solution (mg/g range), which we also found at higher initial concentrations of 1000 ng/L.

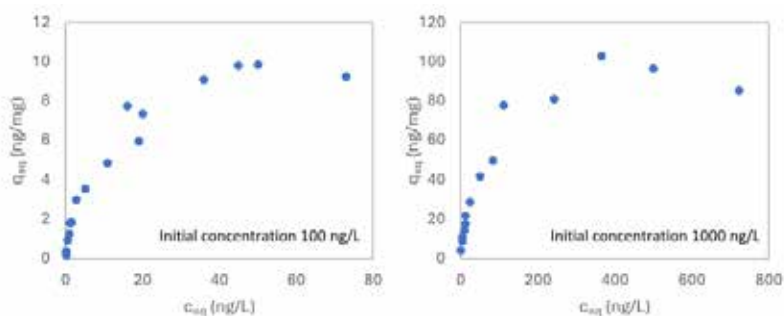


Figure 1: Adsorption of PFAS on activated carbon in batch experiment. Results are shown of PFBS at two different starting concentrations, 100 ng/L and 1000 ng/L. Experiments were conducted with a microporous carbon.

In this presentation, we will discuss the effect of the initial concentration on the adsorption equilibrium, for several different types of PFAS, and at different concentration ranges. We will describe the data with isotherms, and we will discuss kinetic data. Furthermore, we will discuss which mechanisms cause reduced PFAS adsorption at low concentrations.

In scientific literature, typical breakthrough curves are reported, see Figure 2 for an illustrative curve. Typically, breakthrough of PFAS occurs much faster than the breakthrough of other organic micropollutants, resulting in the need for more frequent regeneration of the activated carbon filters.

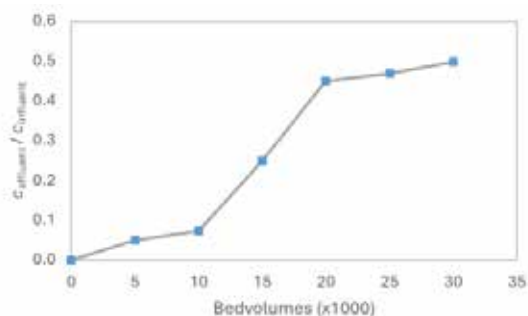


Figure 2: Breakthrough curve of a column experiment for the adsorption of PFOS.

In this presentation, we will discuss, in a quantitative manner, the mechanisms resulting in a fast breakthrough of PFAS in activated carbon filters. We will distinguish and discuss the effect of different types of PFAS, including short-chain and long-chain, with different surface groups. Furthermore, we will discuss the effect of competing components, such as natural organic matter.

To that end, we constructed a theoretical model that includes several processes of relevance in activated carbon columns:

- The adsorption of PFAS on the activated carbon surface. This process is described with an isotherm, which is either a Langmuir, Freundlich or Frumkin isotherm. Isotherm parameters are determined based on equilibrium adsorption experiments.
- The transport of PFAS in the activated carbon granule. This process is described based on surface or pore diffusion, which is physically described using Fick's law. Transport parameters, including the diffusion coefficient, are determined based on kinetic batch experiments.
- The transport of the solution (water) and the solvents (PFAS) in the activated carbon column. This process is described based on convection.

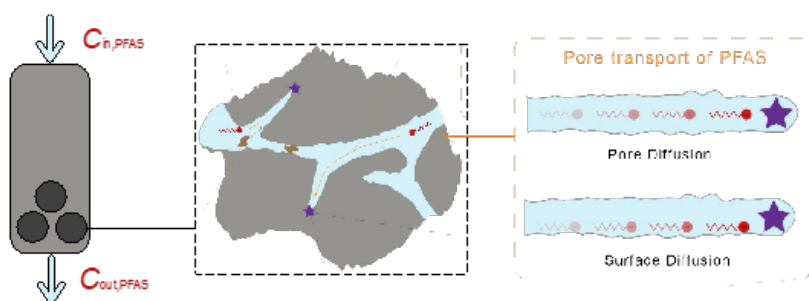


Figure 3: Theoretical model for the analysis of activated carbon columns. Transport in the column and transport in the activated carbon granules are considered.

With this theoretical model, we can elucidate the effects of different process on the breakthrough of PFAS in activated carbon columns. Firstly, we use this theoretical model to describe experimental breakthrough data reported in scientific literature, and secondly, we use this model to evaluate which (combination) of factors results in rapid breakthrough:

- The low adsorption of PFAS on activated carbon in equilibrium.
- The slow transport of PFAS in activated carbon granules.
- Competition with other components.

In this presentation, we will quantitatively discuss the factors resulting in rapid breakthrough, and we will discuss strategies to improve the performance of activated carbon filters.

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Towards the use of mathematical models in predicting the retention of fluoroquinolones in soils

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Keywords: antibiotics; adsorption; soils; regression models.

Abstract

The world population growing leads to the increasing consumption of pharmaceuticals worldwide which can then enter the environment after excretion. Indeed, these emerging contaminants are not completely removed by wastewater treatment plant (WWTP) processes and are thus present in biosolids and WWTP effluents. They can also be present in organic wastes (OW) such as manure or slurry. The application of OW and biosolids as amendment or wastewater reuse for irrigation onto soils contributes thus to their dissemination in the environment.

Among these pharmaceuticals, fluoroquinolones (FQs) are a class of antibiotics of particular interest due to their wide use [1], [2]. Numerous studies have investigated the behavior of FQs in different soil types. Nevertheless, the main soil parameters governing their retention and mobility in soils are still controversial. While some emphasize the role of pH in determining their fate [3], others highlight the significant role of organic matter [4] or soil texture [5].

In this context, the adsorption of two FQs, ciprofloxacin and enrofloxacin for human and veterinary use, respectively, were studied on ten different soils, using the batch technique. To comprehensively understand the factors governing their adsorption on the studied soils, all possible regression models were constructed between the variables (soil characteristics and FQs species) and the adsorbed amounts of FQs. These models were then ranked based on their relative prediction error, estimated by the leave-one-out cross-validation method, evidencing the pertinent parameters of soils/FQs to take into account.

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Generic phosphate affinity constants of the CD-MUSIC-eSGC model to predict phosphate adsorption and dominant speciation on iron (hydr)oxides

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Keywords: iron (hydr)oxides; phosphate; CD-MUSIC model; generic model parameters; database.

Abstract

Estimating the availability of phosphorus in soils and sediments is complicated by the diverse mineralogical properties of iron (hydr)oxides that control the environmental fate of phosphorus. Despite various surface complexation models have been developed, lack of generic phosphate affinity constants ($\log K_{\text{PO}_4}$ s) for iron (hydr)oxides hinders the prediction of phosphate adsorption to iron (hydr)oxides in nature. The aim of this work is to derive generic $\log K_{\text{PO}_4}$ s for the Charge Distribution-Multisite Complexation extended-Stern-Gouy-Chapman (CD-MUSIC-eSGC) model using a large phosphate adsorption database and previously derived generic protonation parameters¹. The optimized $\log K_{\text{PO}_4}$ s of goethite, hematite and ferrihydrite are located in a much narrower range than those in the RES3T database. Specifically, the $\log K_{\text{PO}_4}$ ranges of $\equiv\text{FeOPO}_3$, $\equiv\text{FeOPO}_2\text{OH}$, $\equiv\text{FeOPO}(\text{OH})_2$, $\equiv(\text{FeO})_2\text{PO}_2$, and $\equiv(\text{FeO})_2\text{POOH}$ complexes were 17.40-18.00, 24.20-27.40, 27.90-29.80, 26.50-29.60, and 30.70-33.40, respectively. A simplified CD-MUSIC-eSGC model with species $\equiv\text{FeOPO}_2\text{OH}$ and $\equiv(\text{FeO})_2\text{PO}_2$ and generic $\log K_{\text{PO}_4}$ values 26.0 ± 0.9 and 27.9 ± 0.8 , respectively, provides an accurate prediction of phosphate adsorption and dominant speciation to the iron (hydr)oxides at environmental pH and phosphate levels. For ferrihydrite at low pH and high phosphate levels the species $\equiv\text{FeOPO}(\text{OH})_2$ and $\equiv(\text{FeO})_2\text{POOH}$ cannot be neglected. The simplified model expands the application boundaries of CD-MUSIC-eSGC model in predicting the phosphate adsorption on natural iron (hydr)oxides without laborious characterization.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 32061123007, 42177275, and 42207352) and the Fundamental Research Funds for the Central Universities (No. 2662022ZHQD003).

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Study on multiphase degradation of plastic nanoparticles

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Keywords: nanoplastics; environmental degradation; scanning transmission X-ray microscopy (STXM).

Abstract

Plastic can be found everywhere in the environment and the size of the plastic debris can vary enormously. Nanoplastics, with a size below 1 μm , have been recently found in surface waters [1]. Due to their low density, nanoplastics can float at the surface of water bodies and interact with both oxidants in the gas phase (e.g., ozone), light, and with reactive species (photo)generated in water.

In this study we have investigated chemical composition changes of standard polystyrene nanoparticles under different experimental conditions. Polystyrene nanoparticles dispersed in water have been exposed to light and/or ozone in presence or absence of metals and/or photosensitizers. The chemical changes on nanoplastics have been investigated using the scanning transmission X-ray microscopy coupled to near-edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS). The organic products released in water upon nanoplastic degradation have been identified using a mass spectrometer at high-resolution (HR-MS).

The results showed that partial oxidation of polystyrene particles was observed in all conditions, but in different extend. In particular, in presence of metals or photosensitizers the degradation of nanoplastics was found to be enhanced. Mass spectrometry data highlight that the degradation products release in aqueous phase derive from the breaking of the polymer chain. These results highlight that nanoplastics in the environment could be reactive towards oxidants both in gas phase and in aqueous phase.

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The authors thank the Swiss Light Source (Paul Scherrer Institute) to the access of the facilities (project 20190883 and 20180904). This work is part of a project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program, grant agreement No 948666 – ERC-2020-StG NaPuE, from Fondazione CRT Erogazioni Ordinarie 2020 n. 2020.1874, from MIUR Call FARE project NATtA n. R20T85832Z and PRIN 2022EW9CZN project BIOPLACE.

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The interfacial reaction hotspot in metastable iron minerals: the role and contribution to arsenic immobilization

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Keywords: iron mineral; reaction hotspot; arsenic; immobilization.

Abstract

Iron (Fe) minerals are common constituents of sediments and soils that extensively participate in biogeochemical processes, including adsorption, oxidation, and reduction of nutrients and toxic metals. However, iron minerals in nature are always in a non-thermodynamic equilibrium state due to the seasonal fluctuation of hydrological conditions (e.g., the alternation of dry and wet soil in paddy fields). The transformation of well- to poorly-crystalline iron minerals is a typical process from unstable state to stable state, while its reaction activity such as adsorption capacity for heavy metals also increase. The question is why the reaction activities of metastable iron minerals compared to stable ones increase, and what is the interfacial reaction hotspot in metastable iron minerals. To answer above question, we perform the experiments of hydrothermal aging and surface ion dissolution to simulate iron minerals formation in natural environments. We observed that the transformation of stable to metastable iron minerals produced more vacancy defects, which were the reaction hotspots for the arsenic immobilization. We also established TG-MS-EPR method to quantify the vacancy defect concentration, and reveal the quantitative contribution to the arsenic immobilization. The findings of this study not only help to rational design of highly efficient adsorbents by the strategy of tuning the vacancy defects in the structure of iron minerals, but also provide new insights into understanding the migration and fate of toxic arsenic in soils and sediments.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (41977022), Knowledge Innovation Program of Wuhan-Shuguang Project (2022020801020231), and the Fundamental Research Funds for the Central Universities (2662022YJ017). The authors thank Prof. Yuanzhi Li at Wuhan University of Technology for his help with DFT calculations and Beijing Synchrotron Radiation Facility (BSRF), China, for EXAFS measurements at Beamline 1W1B. They also thank Dr. Hui Yin at the Huazhong Agricultural University for his help in the XAS data analysis.

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Impact of mixed organic compounds on Ni(II) retention in clay rocks: Complexation and synergetic effects

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Abstract

Geological barriers play a crucial role in hazardous waste management and pollution control. Yet they are susceptible to chemical perturbations, such as release of pollutions or chemical co-contaminants, e.g. organic or saline plumes. In France, the Callovo-Oxfordian clay rock is a potential host rock for a long-term radioactive waste disposal. Its high retention capacity limits the transfer of radioactive elements in the geosphere [1]. This study focuses on measurements of radionuclides retention on COx clay rock in the presence of organic plumes, especially the effect of mixed plumes on Ni(II) retention [2,3].

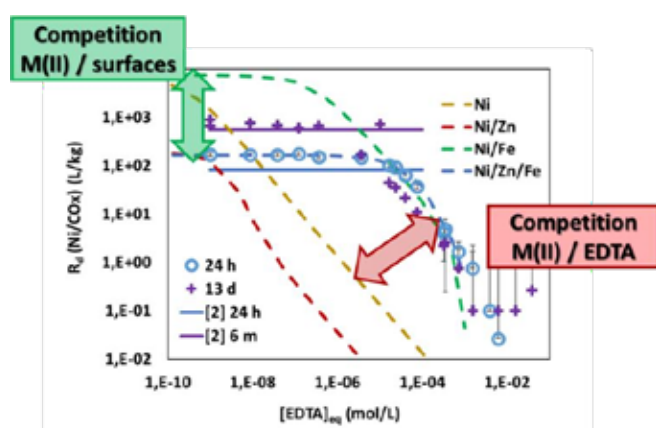


Fig. 1. Sorption of Ni(II) on COx clay rock as a function of EDTA concentration. Experimental data compared with surface complexation models, taking into account co-sorption of various cations.

Despite the apparent simplicity of the binary system (Ni/COx), its interpretation remains challenging. Figure 1 shows a typical retention isotherm, as measured experimentally. The increase in $R_d(\text{Ni})$ over time, at low EDTA concentration (Fig. 1, left part), is due to slow kinetics incorporation. At high EDTA concentration (right part), the formation of $[\text{Ni-EDTA}]^{2-}$ species induces the decrease of $R_d(\text{Ni})$. Moreover, this data illustrates competitive effects between Ni and naturally occurring divalent cations, toward the clay surfaces. Complexation with metals is then shifted both on surfaces and in solution within such ternary systems $\{\text{Ni/EDTA/COx}\}$. We will focus on the development of adsorption models to account for the effect of similar chemical perturbations (phthalate, EDTA, TBP...) and synergetic effects between background major ions. The data presented here for Ni retention may be relevant as an analogue of other divalent ions, in natural media under perturbation by pollution events.

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How to measure and model cadmium availability in tropical soils for low-cadmium sustainable cacao?

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Keywords: bioavailability; cacao; mechanistic assemblage models; simple extractions; soil management

Abstract

Cadmium (Cd) naturally occurs at elevated contents in soils of parts of Latin America, leading to cacao beans regularly exceeding the newly adopted food safety standards for chocolate in the European Union. As such, Cd threatens smallholder farmer livelihoods. Soil reactive surfaces represent an important interface to address this issue, as they govern the solid-solution partitioning of cadmium and the potential uptake by the plant. However, measuring the Cd content is not straightforward, with multiple extractions measuring various fractions of the total Cd pool. Moreover, although geochemical multi-surface models are powerful models to capture and supplement our understanding of the behaviour and fate of Cd in soils, they have rarely been used in tropical perennial systems.

We sampled 34 cacao farms across Colombia with contrasting soil properties, with the objective of explaining Cd content in cacao leaves and beans based on soil geochemistry. First, we developed the isotopic dilution method for uncontaminated tropical soils, using ^{111}Cd as the reference isotope and testing the effect of spike addition on the resulting exchangeable Cd pool (E-value). This method was then compared with simple extractions (HNO_3 , EDTA, DTPA, Mehlich-3) and with the bioavailable pool measured with a 1 mM $\text{Ca}(\text{NO}_3)_2$ extraction. Subsequently, we compared more mainstream empirical models to predict Cd in plants, with using a geochemical multi-surface model including the Non-Ideal Competitive Adsorption (NICA) model for organic matter and the Generalized Two-Layer Model (GTLM) for metal oxides.

We found that regarding the measurement methods, the 1 mM $\text{Ca}(\text{NO}_3)_2$ extraction had the highest predictive value (R^2 0.84), compared to the simple extractions (R^2 0.41-0.46) and E-value (R^2 0.50). Furthermore, the modelled dissolved cadmium concentration with the mechanistic multi-surface model yielded good predictions of Cd in the plant (R^2 0.71-0.79), despite only using basic soil properties (e.g., pH, organic matter content, amount of metal-oxides) and assumptions about soil surface reactivity. The emergence of mechanistic models as powerful low-input tools to predict Cd availability to cacao is valuable, since the low dissolved concentrations cannot always be quantified adequately. Furthermore, such mechanistic models can be used to estimate the potential effect of soil management strategies on Cd uptake, such as the application of lime or compost. Finally, mechanistic models could aid in the identification of expansion areas, where cacao could be promoted as an economically sustainable crop for smallholder farmers.

Hierarchical aggregation of humic nano colloids induced by metal ion binding by small-angle X-ray and neutron scattering

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Keywords: humic substances; aggregation; SAXS; SANS

Abstract

Humic substances (HSs) are an important class of natural organic matters, affecting the fate of pollutants and nutrients in soil and aquatic environments. They are not molecular entities with distinct structures but can be considered as collections of organic molecules with certain physicochemical properties in common. Aggregation and disaggregation of HSs are vital processes that affect the environmental 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, their aggregation structures in nano- and meso-length scales are poorly understood. Recently, we have revealed the heterogeneous aggregation of humic nano colloids induced as a pH change. [1] The objective of this study is to further elaborate the aggregation structures of HSs. Both small-angle scattering of X-ray and neutron was employed to get insights on heterogeneous aggregation of HSs, induced by the binding of metal ion with different valency.

HS examined in this study was HA commercially available from Sigma-Aldrich (PAHA). The samples for small-angle X-ray scattering (SAXS) and neutron scattering (SANS) were prepared at 2 g/L in D₂O (>99.8%) at pD = 6 in the presence of 5 mM NaCl and different concentrations of Ca²⁺, Fe³⁺, and Zr⁴⁺. The concentrations of the metal ions were chosen, based on their binding amounts. 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 spallation neutron source. The SAXS measurements were carried out at the BL-6A of the photon factory, KEK (Tsukuba, Japan) with monochromized X-ray at $\lambda = 1.5 \text{ \AA}$.

The SANS profiles of PAHA remain unchanged regardless of the presence of the metal ions and their concentrations, which was in line with the SANS results of PAHA at different pD [1]. This suggests that relatively large aggregates made of proton-rich shells of primary particles of PAHA were intact even after binding of multi-valent metal ions. On the other hand, the SAXS profiles exhibited the progress of aggregation of electron-rich cores of PAHA primary particles, depending on both the metal ions and their concentrations.

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Uptake/Release Kinetics of Metal Ions and Organic Molecules by Micro- and Nano-Plastics

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Keywords: transient flux; intraparticulate diffusion; polymer aging.

Abstract

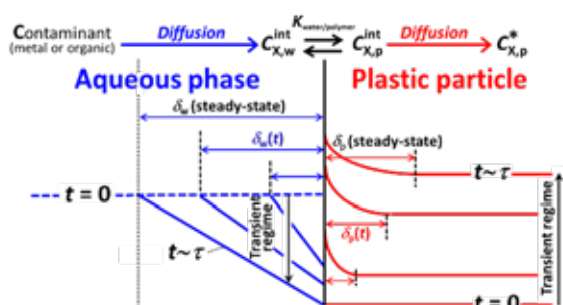


Fig. 1. Transient and intraparticulate diffusion processes which govern contaminant accumulation kinetics in micro/nanoplastic particles.^[1]

Plastic particles in aquatic systems carry a cargo of associated inorganic and organic contaminants, comprising polymer additives as well as environmentally acquired compounds. The uptake/release kinetics of such particle-associated contaminants will depend on the particle size/geometry, extent of polymer degradation, as well as the prevailing physical and chemical conditions. Mechanistic knowledge of the involved processes is fundamental for understanding the bioavailability of particle-associated contaminants. We present a theoretical framework (shown schematically in Fig. 1) to describe the uptake and release kinetics of metal ions and organic compounds by plastic particles and apply it to the analysis of experimental data for pristine and aged micro- and nano-plastic particles [1]. Notably, we elucidate the contribution of transient processes to the overall kinetics of plastic reactivity towards aquatic contaminants. Intraparticulate contaminant diffusion is found to be of paramount importance in defining the kinetics of contaminant absorption by micro-/nano-plastic particles.

Upon polymer aging, the relationship between the changes in the equilibrium water-polymer partition coefficient, $K_{w,p}$, and the diffusion coefficient of the target compound, X , in the polymer phase, $D_{X,p}$, is rather consistent across all data. In broad environmental context, aged plastics tend to be ingested by aquatic organisms more frequently than pristine ones, but there are disparate reports on the relative bioavailability of the associated compounds. Mechanistically-based environmental risk assessment of micro- and nano-plastics calls for coupling the dynamic nature of particle-based processes with those occurring within biota.

Acknowledgments

RMT acknowledges funding from the FWO (projects G053320N and G060920N), BELSPO (B2/20E/P1/RESPONSE), and the Universiteit Antwerpen Bijzonder Onderzoeksfonds (SEP-BOF 2020).

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Role of self-filtration in the deposition of fragments: the case of micro- and nanoplastics

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Keywords: Transport; Aggregates; Ripening; Kinetics; Particle-particle interaction.

Abstract

It is still unclear how the properties of particulate contaminants impact their mobility through porous media such as filters, soils and aquifers due to i) poor environmental relevance of the model particles that are studied and ii) the use of packed bed experiments which do not allow a direct observation of deposition dynamics. For example, while environmentally occurring microplastics (MPs, 1 mm to 5 mm) and nanoplastic (NPs, <1 mm) typically display irregular shapes, rough surfaces and polydisperse sizes, most particles studied are spherical, smooth and monodisperse in size (e.g.: Polystyrene Latex (PSL) spheres).

In a sand column with repulsive conditions, we previously demonstrated enhanced deposition of rough PS fragments with irregular shapes and with a size continuum (10 nm to 5 mm) compared to PSL spheres. Furthermore, the size fraction <300nm was preferentially transported¹. Therefore, we hypothesized that i) size-dependent deposition rates and/or ii) particle-particle interactions were occurring.

In this work, we investigate the deposition mechanism of these PS fragments at the pore scale using a transparent 2D porous media in repulsive conditions. Particle deposition as a function of size was monitored with a combination of in-situ and ex-situ measurements: optical microscopy (in-situ), absorbance spectroscopy, Coulter counter and dynamic light scattering measurements (ex-situ).

In the absence of natural organic matter (NOM), micrometric particles rapidly deposit and promote the physical interception of smaller nanoparticles by creating local porous roughness or obstacles. In the presence of NOM, differences according to particle size were no longer observed and all fragments were more prone to being re-entrained, thereby limiting the growth of deposits. This work shows that the pore surface roughness and porosity of the pore surface, which are generated by deposited particles, enhance the deposition of inflowing colloidal particles, especially in the absence of NOM. This demonstrates that even in fully repulsive conditions, particles can be deposited in porous media by hydrodynamic forces. Overall, this study helps to better understand the filtration of particles with polydisperse sizes and heterogenous shapes, which are ubiquitous in nature.

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Interface between polyethylene terephthalate microplastics and microbiota activity in the ruminal environment

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Keywords: microplastics; polyethylene terephthalate; ruminal environment; degradability and fermentative activity.

Abstract

Microplastics (MPs) enter the animal digestive system through contaminated feeds [1, 2] creating a unique interface between the rumen and microbiota, resulting in MPs degradation [2-4]. This study investigated the interaction between polyethylene terephthalate (PET) and ruminal activity to understand its influence on feed degradation and fermentation processes.

Table 1. Effects of PET contamination in feed on the *in vitro* ruminal activity.

PET %	pH	NH ₃ -N mg/100mL	DMD mg/g	OMD mg/g	Protozoa 10 ⁵ /mL	PF
0	6.54	24.90 ^b	671.9 ^a	721.2 ^a	4.38 ^a	2.272 ^a
0.6	6.56	25.51 ^{ab}	666.8 ^{ab}	712.1 ^{ab}	4.18 ^a	2.164 ^b
1.2	6.56	25.70 ^a	652.7 ^{bc}	697.7 ^{bc}	4.24 ^a	2.077 ^c
1.8	6.53	26.56 ^a	644.4 ^c	688.3 ^c	3.87 ^b	2.057 ^c
SEM	0.041	1.022	9.36	9.99	0.235	0.0392

^{a-c} Within a column, different superscripts differ significantly (P < 0.05).

The experiment was conducted using an *in vitro* gas production (GP) system with lamb rumen fluid and buffer solution to evaluate the effects of different doses of PET contamination (0, 0.6, 1.2, 1.8% dry matter of feed) in 200 mg of concentrate on: pH; GP at different times (at 0, 2, 4, 6, 12, 24, 48, 72 and 96 hours); rumen ammonia-nitrogen (NH₃-N); dry and organic matter degradability (DMD, OMD); rumen protozoa; and microbial efficiency (PF). The experiment was triplicated and repeated over three consecutive weeks.

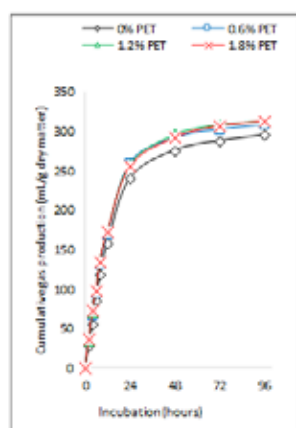


Figure 1. Effect of PET on the *in vitro* GP.

The presence of PET in concentrate feed within the lamb ruminal environment negatively affected degradability and fermentative processes, particularly at the highest dose. Compared to the control feed without PET addition, PET decreased DMD, OMD, ruminal protozoa, and PF (Table 1), while it increased ruminal GP (Figure 1) and NH₃-N.

The study demonstrated an interaction between PET and ruminal microbiota. These findings highlight the potential adverse impacts of PET on the ruminal fermentation and feed degradability. Further research is needed to explore the effect of PET on gastrointestinal activity and to develop strategies to mitigate the adverse effects.

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pH-dependent contaminant availability in relation to reactive surface (trans)formation during field scale sediment ripening

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Keywords: dredged sediment; ripening; environmental safety; surface (trans)formation

Abstract

The beneficial application of (ripened) dredged sediments, e.g. in construction, is hampered by uncertainty about contaminant availability and chemical stability over time. We hypothesised that the (trans)formation of reactive surfaces in these sediments during ripening affects contaminant availability. Our study focused on an ongoing field scale experiment where dredged harbour sediment is stockpiled in order to dewater and ripen. Additionally, historically applied dredged sediments from the same harbour were sampled resulting in a multidecade ripening sequence of material from similar origin.

The development of both mineral and organic reactive surfaces in these samples with increasing stockpiling or historical age was quantified. The reactivity of solid and dissolved organic matter was characterised by fractionation of operationally defined humic fractions [1]. Extractions targeting the formation and crystallinity of iron-, aluminium-, and manganese(hydr)oxides [2] were coupled with an adsorption isotherm approach to determine the effective reactive surface area of metal(hydr)oxides [3]. Contaminant solubility was assessed under controlled pH conditions ranging from 2 to 12 in order to mechanistically study the release in relation to the reactive surface composition. The concentration of major and trace elements in addition to dissolved organic carbon and aforementioned humic fractions in solution were determined for each pH.

Preliminary results show temporal changes in the composition and solubility of mineral and organic reactive surfaces. The release of contaminants is several orders of magnitude higher at the pH-extremes compared to circumneutral conditions, which appears to be strongly associated with the dissolution of the reactive surfaces (figure 1). Thus, the pH-dependent solubility of contaminants and reactive surfaces in combination with characterisation of surface binding capacity gives valuable insights in the developments of contaminant-surface interactions during sediment ripening. These solid-solution partitioning mechanisms will be further studied using multi-surface speciation modelling.

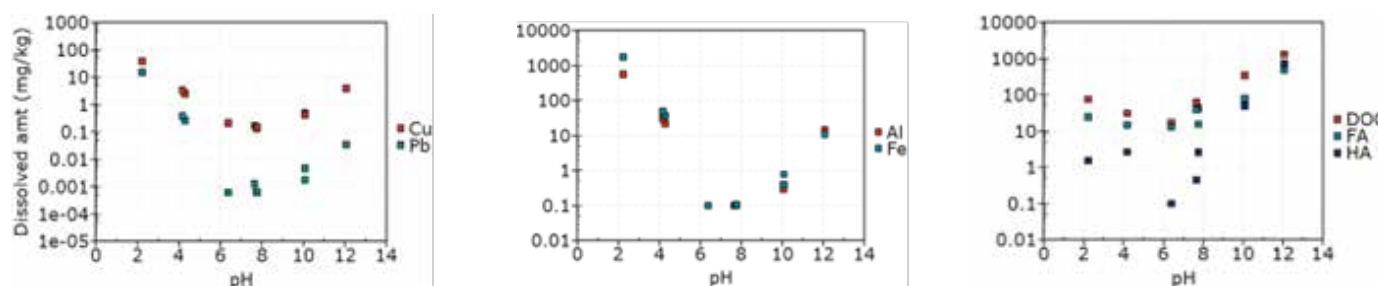


Figure 1: pH-dependent dissolved amount in mg per kg of dry material for copper and lead (left) compared to iron and aluminium (centre) and dissolved organic carbon (DOC) including humic acid (HA) and fulvic acid (FA) (right)

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Interfacial reactions affecting the Cs leaching behaviors of adsorbents solidified with cement and geopolymer

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Keywords: Cs; stabilization; cement; geopolymer; leaching behavior

Abstract

The atmospheric release of ¹³⁷Cs caused by the accident at the Fukushima Daiichi nuclear power plant in 2011, Japan, resulted in decontamination works of topsoils and disaster wastes to rehabilitate the contaminated areas. Among the wastes collected at the interim storage facility in Fukushima prefecture, combustibles are incinerated to reduce their volumes. ¹³⁷Cs are majorly concentrated in fly ash after incineration. Such fly ash with ¹³⁷Cs is readily soluble, so further washing and adsorbing on sorbents such as zeolite and ferrocyanide are considered, which can be further stabilized by binders such as cement or geopolymer, for the final disposal. Geopolymer-solidified zeolite is known to undergo some phase alteration¹ that could increase the Cs immobilization ability.

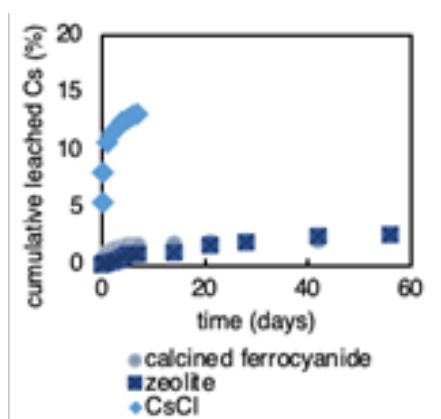


Fig1. Cumulative leached fraction of Cs in geopolymer solidified forms of different Cs adsorbents and CsCl.

The long-term leaching behavior of ¹³⁷Cs from such solidified forms must be evaluated for safety assessment and waste disposal site design. This study aims to understand the long-term leaching behavior of ¹³⁷Cs through leaching experiments following the ANSI/ANS-16.1 standard. The fixation and leaching mechanisms of ¹³⁷Cs will also be assessed with the understanding of the speciation and the distribution of Cs in the solidified forms, especially focusing on those at the interfaces of the adsorbents and binders and the leachate. The abovementioned target solidified forms were prepared together with cement and geopolymer with the addition of CsCl as a reference. Solution compositions of the leachate, the distribution of Cs and major elements of the solidified forms, and the surrounding chemical environments of Cs in the solidified forms were investigated using ICP-OES, ICP-MS, SEM, and XAFS.

The result of the Cs leaching experiment (Fig.1) shows the existence of zeolite and calcined ferrocyanide reduce the leaching fraction of Cs in comparison to the CsCl addition to the binder. Such differences are suggested to result from the conserved sorbent's function to retain Cs, and alteration of the sorbents due to the mixing with the binders, which will be discussed in detail with the support of the solid-phase analyses.

Acknowledgments

This research was performed by the Environment Research and Technology Development Fund (JPMEERF22S20910) of the Environmental Restoration and Conservation Agency provided by the Ministry of the Environment of Japan.

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Degradation of chrysotile asbestos in soil

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Keywords: mineral weathering; tetrahedral iron; hydroxyl radical yield; cement; pH; plant root exudates.

Abstract

Chrysotile is an asbestiform mineral that has been widely used for its favorable physical properties. In most European countries its use has been banned due to its carcinogenicity upon inhalation resulting from its ability to generate hydroxyl radicals through Haber-Weiss cycling of tetrahedral Fe at the fiber surface. However, large quantities of chrysotile have ended up in the environment e.g. as a result of application of asbestos cement waste for road construction, and illegal dumpings. This raises questions regarding the environmental fate and associated risks of chrysotile asbestos in soils, including: Does chrysotile degrade in soils and how does degradation affect its hazard? How are degradation and hazard affected by soil properties and the presence of cement? And can chrysotile weathering be enhanced by root exudates from plants?

To address these questions a 2.5-year pot trial experiment was performed with three soils covering a wide pH-range. Three plant species (sorrel, lupine and Kentucky bluegrass) with specific root exudate characteristics were included. Chrysotile was buried at the bottom of the pots, embedded between two membrane filters glued together. Treatment with and without plants and cement addition were included. Pots were harvested after 0.5, 1, 1.75 and 2.5 years. Composition and reactivity of the soil solid phase, soil solution and chrysotile fibres were thoroughly characterized by various extraction protocols, fusion digestion, and EPR spin-trapping.

Our results demonstrate that chrysotile is subject to weathering in soil environments. The weathering rate proved strongly soil-dependent, and was largest in the soil with the lowest pH. In comparison to batch experiments with chrysotile suspensions of the same pH, weathering rates were up to an order of magnitude slower in the pot trial. The presence of cement inhibited chrysotile weathering by raising the pH. Our study showed no evidence that plant root exudates significantly enhance the weathering rate. During weathering the potential of chrysotile to produce hydroxyl radicals became reduced, but the reduction was not proportional to the weathering rate. The hydroxyl radical yields declined throughout the trial down to approximately 30% of their initial value, except in the most acidic soil. There the radical yield first decreased, but eventually increased again up to about 65%. The presence of cement slowed down the rate of decline in radical yield.

Our findings provide support for soil remediation strategies for asbestos based on natural attenuation. However, the time required for remediation will strongly depend on soil properties, particularly the soil pH, and the presence of cement.

An in-situ method of SEM-EDS combined with image processing to evaluate the speciation and transformation of Cu and Pb in contaminated soil

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Keywords: SEM-EDS; image processing; Cu; Pb speciation and transformation; organic-mineral interface.

Abstract

Developing alternative approaches to chemical extraction methods is crucial for the speciation evaluation and risk assessment of heavy metals in contaminated soils. Based on scanning electron microscope –energy dispersive spectrometer (SEM-EDS) and image processing, we established an in-situ non-destructive technique to quantify the speciation and transformation of Cu and Pb in an abandoned contaminated soil which was incubated with three different organic matters for 60 days. Particle size fractions of < 2 mm, 2-20 mm, and 20-53 mm were further divided by image processing to investigate the distributions of Cu and Pb in different soil aggregates. The overlay mapping among elements such as C, O, Fe, Al, Si, Ca, Cu, Pb informed by SEM-EDS were employed to analyse and differentiate the species of Cu and Pb associated with different soil constituents including organic matter, Fe oxides, aluminosilicates, and carbonates. After incubation, the organic matter bound Cu and Pb were increased by 10.2% - 12.5% and 11.4% - 13.9%, while the Fe oxides bound Cu and Pb were decreased by 9.3% - 11.3% and 11.0% - 12.5%, respectively. The variations in soil organic and Fe oxides bound Cu and Pb were affirmed by the data of X-ray absorption fine structure (XAFS). Some minor changes were observed for the carbonates bound (increases by 1.8% - 3.3%) and the aluminosilicate bound Cu and Pb (decrease by 2.4% - 4.6%). The results indicate the transformation of aluminosilicates and Fe oxides bound metals to organic matter and carbonate bound species after the input of three organic matters. Moreover, the increases of organic matter bound Cu and Pb were mainly found in the < 2 mm soil particles. This study provides an effective, eco-friendly, and time-saving technique for the estimation of heavy metal speciations and understanding their transformation at the organic-mineral interfaces in polluted soils.

Acknowledgments

This work was financially supported by the National Key Research and Development Program of China (2020YFC1806803).

Glyphosate speciation at the goethite interface: insights from surface complexation modelling and competition

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Keywords: glyphosate; goethite; surface speciation; CD-MUSIC modeling.

Abstract

Adsorption of glyphosate to metal (hydr)oxides determines its environmental fate [1], [2]. However, its surface speciation is a notoriously complex problem due to the many functional groups and corresponding charge behaviour. The binding of glyphosate to goethite, the most common crystalline iron (hydr)oxide, is extensively studied with spectroscopic methods [3–5] but the reported surface speciation from these techniques varies widely between publications. With this study, we provide new insights through experimental data collection and state-of-the-art mechanistical surface complexation modelling.

Glyphosate adsorption to well-defined goethite was measured over a wide range of concentrations and pH. We used the multi-site complexation (MUSIC) model combined with the charge distribution (CD) approach to model the data, complemented with MO/DFT geometry optimization of the surface complexes to constrain the charge distribution coefficient at the surface. The model indicates a speciation depending on pH and loading. Glyphosate bind to goethite via its phosphonate group, forming both binuclear bidentate and monodentate surface complexes, with the bidentate being the most prominent (>60%). The amine in glyphosate bound as a bidentate surface complex partially deprotonates at high pH. The monodentate complex has a protonated amine over the entire range, but shows an additional protonation of the phosphonate at low pH and high surface loadings. The model gives a consistent, mechanistic and quantitative understanding of glyphosate binding to goethite and its variation with pH and surface loading. In addition, competition with the important environmental compounds phosphate and humic acids can be well predicted. These results are of high value for an improved prediction of glyphosates fate in environmental systems.

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PFOA and PFOS binding onto Goethite: Experimental results and modelling with the Charge Distribution and Multi-site Complexation (CD-MUSIC) Model

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Keywords: PFAS; Adsorption; Surface complexation; Goethite; CD-MUSIC model.

Abstract

Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the two most commonly found per- and polyfluoroalkyl substances (PFAS) in soil. PFAS binding in soils is strongly related to organic matter, but also metal oxides were found to contribute¹. In metal oxides-water interface, electrostatic interactions are considered the most important adsorption mechanism for PFOS and PFOA^{2,3,4}. The surface charge of goethite, a common iron oxide in soils, is pH dependent. In addition to pH, the charge depends on specific adsorption of anions and cations, like phosphate and calcium which are commonly present in soil and water, as well as on the ionic strength. Therefore, in the current study, PFOA and PFOS adsorption on goethite was investigated by batch experiments for a range of pH at three ionic strengths and in the absence and presence of phosphate and calcium ions. The results of batch experiments indicate an increase in PFOA and PFOS adsorption with decreasing pH, attributed to increasing positive charge on the goethite surface, enhancing the attraction of negatively charged PFOA and PFOS molecules. PFOA adsorption decreased with increasing ionic strength throughout the experimental pH range, whereas PFOS adsorption decreased at higher ionic strength at low pH but increased at higher pH (pH > 6.5). In the presence of phosphate, adsorption of PFOA and PFOS decreased, while the presence of calcium increased their adsorption, particularly at higher pH ranges (pH > 7). These findings were interpreted by using the CD-MUSIC model that has been developed for the adsorption of inorganic ions (e.g. phosphate and calcium). Preliminary model results considering electrostatic interactions and specific adsorption are able to describe the effect of pH, ionic strength, and the competing/synergistic ions. To model the dependence of adsorption on PFOA loading we had to assume only a small fraction of the goethite being involved in PFOA binding which is not yet understood and needs further investigation.

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Microplastics identification in biosolids: application of NIR spectroscopy coupled with multivariate statistics

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Keywords: Microplastics; Biosolids; NIR spectroscopy; Multivariate statistics.

Abstract

Microplastics (MPs, particle size less than 5 mm) are considered emerging pollutants and they are ubiquitously present in the environment. MPs come from a variety of sources such as personal care products, wastewater treatment plants, textile washing and agricultural practices. In soil, MPs can have different effects, from physico-chemical alterations to decreasing of the enzyme activity and microbial diversity [1]. The occurrence of MPs in soil environments is primarily investigated through chemical extraction. However, this method is time-consuming and thus not suitable for large-scale evaluations. NIR spectroscopy is a promising tool for rapid monitoring of plastics in complex matrices such as organic fertilizers and compost [2]. In a previous work [3], we analyzed biosolid samples from 6 different wastewater treatment plants and found that on average, biosolids contained 0.1–0.4 g of plastics (size more than 2 mm) per kg. Moreover, the use of using NIR and ATR-FTIR spectroscopy, which allowed us to identify and confirm the presence of some of the most common polymers, such as PE, PET, PP and PLA. In this research we aim to study the distribution of MPs in biosolid matrices and to test the approach of NIR technology coupled with a machine learning algorithm for the rapid quantification of MPs, based on a prediction model. Additionally, we provide SEM-EDS observation of biosolids to ensure in-depth analysis and confirmation of MPs. The initial results showed that NIR spectroscopy can distinguish aged plastic debris from biosolids background. Jointly, we aim to provide further information about the quantity of MPs in the investigated biosolids, as well as possible application of NIR spectroscopy for rapid MPs detection in soil. This could help us establish more effective and faster identification and quantification of MPs, thus be able to identify pollution hotspots and develop corresponding remediation strategies.

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Iron mineral surfaces and their impact on pollutant attenuation in acid mine drainage

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Keywords: mineral surfaces; adsorption; modelling; acid mine drainage.

Abstract

Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the two most commonly found per- and polyfluoroalkyl substances (PFAS) in soil. PFAS binding in soils is strongly related to organic matter, but also metal oxides were found to contribute¹. In metal oxides-water interface, electrostatic interactions are considered the most important adsorption mechanism for PFOS and PFOA^{2,3,4}. The surface charge of goethite, a common iron oxide in soils, is pH dependent. In addition to pH, the charge depends on specific adsorption of anions and cations, like phosphate and calcium which are commonly present in soil and water, as well as on the ionic strength. Therefore, in the current study, PFOA and PFOS adsorption on goethite was investigated by batch experiments for a range of pH at three ionic strengths and in the absence and presence of phosphate and calcium ions. The results of batch experiments indicate an increase in PFOA and PFOS adsorption with decreasing pH, attributed to increasing positive charge on the goethite surface, enhancing the attraction of negatively charged PFOA and PFOS molecules. PFOA adsorption decreased with increasing ionic strength throughout the experimental pH range, whereas PFOS adsorption decreased at higher ionic strength at low pH but increased at higher pH (pH > 6.5). In the presence of phosphate, adsorption of PFOA and PFOS decreased, while the presence of calcium increased their adsorption, particularly at higher pH ranges (pH > 7). These findings were interpreted by using the CD-MUSIC model that has been developed for the adsorption of inorganic ions (e.g. phosphate and calcium). Preliminary model results considering electrostatic interactions and specific adsorption are able to describe the effect of pH, ionic strength, and the competing/synergistic ions. To model the dependence of adsorption on PFOA loading we had to assume only a small fraction of the goethite being involved in PFOA binding which is not yet understood and needs further investigation.

Acknowledgments

The work was supported by Xunta de Galicia - Consellería de Educación e Ordenación Universitaria (Consolidation of Competitive Research Groups; GI-1245, ED431C 2022/40)

New insights from the International GEOTRACES Programme on impacts of ocean boundaries and particle dynamics on ocean trace element biogeochemistry

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Keywords: trace elements; ocean biogeochemistry; ocean boundaries; particles; GEOTRACES.

Abstract

The world's oceans play a key role in the earth climate system. Oceans take up large amounts of atmospheric CO₂ through physical and biological processes, and thereby buffer climate change. The supply of macro-nutrients, including phosphorus, nitrogen and silicic acid controls the productivity of phytoplankton in the ocean and consequently the ocean CO₂ uptake by biological processes. In recent years it has become clear that a low supply of iron can limit productivity in about 40% of the world's oceans. Furthermore, important roles in controlling ocean productivity for cobalt, manganese and zinc have recently been demonstrated. These trace elements are essential for phytoplankton in various biochemical roles and thus serve as micronutrients.

The International GEOTRACES was initiated in the mid-2000s and has as aim to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes (TEIs) in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions.

As part of GEOTRACES a host of research cruises has been conducted in ocean basins along zonal sections to determine in detail the distributions, sources and sinks of TEIs in the water column. Our team has been leading a range of GEOTRACES activities, where we combine the use of TEIs as tracers for flux processes (e.g. helium isotopes for hydrothermal inputs, aluminum for atmospheric inputs, manganese and radium isotopes for benthic supply) to investigate the biogeochemical cycling of TEIs, and their interactions with surface ocean productivity and the carbon and nitrogen cycles (incl. diazotrophy). This presentation will report on our findings in the world's oceans and highlight the critical roles of TEIs in the present and future oceans. The role of scavenging and release of trace elements by particles in the ocean will be highlighted using trace element additions and removal along large scale water mass transport routes. In addition, the role of TEI additions along ocean boundaries (rivers, atmosphere, shelf sediments, hydrothermal vents) will be assessed in a mechanistic and quantitative manner.

Acknowledgments

We acknowledge funding by the German Science ministry (BMBF), the German research council (DFG), GEOMAR, and the UK research council (NERC) for our research activities.

Advanced Methods to Detect and Image Microplastics and Nanoplastics in Whole Organisms

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Keywords: nanoplastics; biouptake; imaging; detection; microscopy.

Abstract

A key challenge in understanding the environmental burden of microplastics and nanoplastics is their detection in complex carbon-rich natural matrices such as soils or whole organisms. We have been working on the development of new plastic labeling and imaging techniques for detection of nanoplastics and microplastics in environmental samples. The first approach relies on stimulated emission depletion microscopy (STED) to detect labeled nanoplastics in whole organisms or other complex samples [1]. A second approach circumvents the need to label the plastic particles by implementing a tissue clearing technique to image the particles while preserving the structure of the whole organism [2]. This presentation will describe the new methodologies and provide examples of microplastic and nanoplastic detection and localization in representative aquatic and terrestrial organisms. We will demonstrate the versatility of these advanced imaging techniques for detection of the smallest plastics in complex environmental samples.

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In-situ application of the active-passive sampling (APS) technique for monitoring psychoactive compounds in wastewater

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Keywords: Active-passive sampling; wastewater analysis; psychoactive compounds; HLB sorbent; solid-phase extraction.

Abstract

The applicability of active-passive sampling (APS) technique was evaluated in the effluent of a wastewater treatment plant (WWTP) in Belgium. APS integrates both active and passive sampling approaches, employing a pump to facilitate a controlled laminar flow of the sampled medium across a diffusion cell with selective receiving phases. The APS device was equipped with Hydrophilic-Lipophilic Balanced (HLB) and Mixed-mode Cation Exchanger (MCX) sorbent phases for the in-situ preconcentration of psychoactive compounds (i.e., opioids, antidepressants, and drugs of abuse). The performance of the APS was assessed across five sampling periods by comparing the measured water concentrations (cw, μM) with those obtained from daily 24-h composite sampling followed by solid-phase extraction (SPE) and conventional passive sampling using organic diffusive gradients in thin films (o-DGT). Aqueous concentrations of hydroxybupropion, O-desmethylvenlafaxine, N-desmethylcitalopram, morphine, and benzoylecgonine by APS were in good agreement compared to both SPE and o-DGT (generally <40% difference). However, EDDP and trazodone concentrations by APS and o-DGT were 2-3 times higher compared to SPE values while APS concentrations of tramadol were ~50% lower compared to SPE and DGT. The difference in concentrations may be attributed to the associations of the compound species to the micro- and nanoparticles in wastewater, which could affect their rate and extent of sorption to the sorbents. Overall, the APS technique demonstrates potential for an alternative method for wastewater-based epidemiology, highlighting the necessity of investigating compound-particle interactions typically overlooked in traditional approaches.

Acknowledgments

This study was conducted with the financial support from the Research Foundation - Flanders (FWO) grants G060920N and 1148622N.

Chitosan-based passive samplers for the analysis of norovirus in water by adsorption and desorption

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Keywords: chitosan; norovirus; adsorption; desorption; passive sampler.

Abstract

Human noroviruses are the leading cause of acute gastroenteritis in humans worldwide. Monitoring them in water is difficult because the components of the environmental matrix can inhibit virus genome analysis techniques (RT-qPCR).

The aim of this study is to design an environmentally friendly passive sampler based on porous materials that combines good affinity for adsorption of viruses in wastewater and drinking water, with reversible properties enabling viruses to be desorbed for quantification by RT-qPCR analysis.

Chitosan (CS)-based adsorbents were prepared by gelation of acidic solutions of CS (2-3.5 mass.%) in a NaOH solution: (i) hydrogels (HCS) in the form of beads (\varnothing : 2.3-3 mm; S_{BET} : 50-70 m².g⁻¹) and films (thickness: 0.5- 2 mm, S_{BET} : 7 m².g⁻¹); (ii) beads obtained by Cu²⁺ ionic printing (CS-I) (S_{BET} : 4 m².g⁻¹). Scanning Electron Microscopy (SEM) observation of the materials confirmed the pore size distribution (HCS beads: $\lambda_{\text{epore}} \sim 30-50$ nm) determined by the Barrett-Joyner-Halenda (BJH) method [1]. For all HCS, the value of the isoelectric point measured by zetametry is 7.

The adsorption and desorption of Murine NoroViruses ("MNV", non-pathogenic viruses for humans, used as a model for human noroviruses, $\varnothing \sim 35$ nm) were studied in saline water (NaCl 0.1 mol.L⁻¹), drinking water and in wastewater from the outlet of a wastewater treatment plant (Chambéry, France). The desorption of MNVs captured on HCS beads and films was studied using solutions of different ionic strengths (NaCl 0.1-4 mol.L⁻¹), as a function of pH (7-9), surfactant concentration (Tween20 0.005-0.5%), temperature (25-60°C), time (0.5-4 h) and adsorbent mass (0.1-1.0 g).

MNV adsorption kinetics in saline water (C_0 : 10⁸ ug.mL⁻¹, dry material mass: 10 mg) showed MNV adsorption efficiency of 85% on HCS beads and films, $\sim 27\%$ on CS-I, after 2 h contact time. In all cases, an equilibrium plateau was reached after 6 h of adsorption. Under optimal desorption conditions, up to 91% of the MNV adsorbed on HCS beads (in NaCl 0.1 mol.L⁻¹) are recovered after 2 h. The desorption method becomes less effective as the amount of material used for adsorption increases. In drinking water and wastewater, $\sim 60-70\%$ and 0-13% of MNVs were recovered ($\sim 80\%$ adsorbed) respectively, indicating that the method is sensitive to the composition of the media.

Porous HCS have suitable properties (pore size, surface charge, specific surface area) for the adsorption of MNV in water. By adjusting the physico-chemical parameters of an elution solution, a significant amount of virus ($> 60\%$) can be recovered by desorption representative of the amount adsorbed on the material. The automatic passive sampling of spiked MNV in wastewater using HCS beads was then tested.

Acknowledgments

Auvergne-Rhône-Alpes Region (France) for supporting the « VIROCAPTUR » Pack Ambition Recherche Project.

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Extraction of inorganic nanoparticles from soils and their characterization by single particle ICP-MS

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Keywords: Nanoparticles; Agricultural Soil; Sediment; Sludge, Single Particle ICP-MS.

Abstract

With increasing uses of nanomaterials (e.g., Ag, CeO₂, SiO₂, TiO₂, and ZnO) in diverse applications (cosmetics, pharmaceuticals, agriculture, semiconductors, etc.), it is necessary to assess their potential impact on the environment. Such an assessment involves better understanding the fate and behavior of nanoparticles (NPs) in complex environmental matrices, such as soils, which depends on challenging analytical strategies and advanced instrumentation to ensure data quality and reliability. Indeed, unlike in water, where generally only dilution is required, the direct analysis of nanoparticles in soils using single particle detection techniques is very difficult. We will discuss two approaches of extracting nanoparticles from soils and the use of two different inductively coupled plasma mass spectrometers for single particle measurements: double focusing magnetic sector field (ICP-SF-MS) and a time-of-flight (ICP-TOF-MS). Metal containing nanoparticles (M-NPs) were extracted from different types of soils, including river sediment, agricultural soil, and industrial and domestic sludges. Ultra-pure water was used as the simplest/soft extraction solution to simulate mobility of M-NPs in wet soil, whereas Na₄P₂O₇ was a more effective extractant to maximize the detection of less abundant particles. Ultrasound assisted continuous flow extraction (USCFE) was compared to a standard batch extraction (BE) procedure. The results showed that the latter was time consuming and less effective than the continuous flow extraction. It was found that at least 5 successive extraction cycles of 18 hours each were needed for BE to achieve optimal extraction of Si-NPs (ca. 6 × 10⁹ NPs/mg), while relatively same high numbers of particles could be extracted by USCFE in about 3 hours. Due to its high sensitivity, ICP-SF-MS allowed single-element-single-particle measurements of the smallest detectable M-NPs (e.g., 28 nm SiO₂, 16 nm TiO₂, and 11 nm Al₂O₃) in soil extracts. On the other hand, with its multielement-single-particle capability, ICP-TOF-MS led to valuable information about the particle composition. For instance, among the detected Si-NPs in the agricultural soil, 34 % were likely SiO₂ NPs, while the largest proportion was composed mostly of aluminosilicates (26 % Si-Al-NPs, 18 % Al-Si-Fe-NPs, 9 % Si-Fe-NPs, 5 % Al-Si-Ti-Fe-NPs, and smaller amounts of other multielement-NPs). Although the obtained particle compositions do not include non-measurable elements (i.e., C, N, O, and S) by the used techniques, the elemental composition of each nanoparticle could eventually be used to help distinguish engineered and naturally occurring M-NPs, as well as their potential interactions with the soils. We believe that the collection of reliable data from single particle (ICP-SF-MS and ICP-TOF-MS) analyses will be of great benefit to studying the behavior and environmental impacts of nanomaterials.

POSTER PRESENTATIONS

Valorization of spent coffee grounds as soil amendment and valuable bio-additives

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Abstract

Spent coffee grounds (SCGs), a primary by-product of coffee processing, hold potential as a soil amendment material due to their high organic matter and nutrient content. However, direct soil application can result in detrimental ecotoxicological effects caused by the presence of phytotoxic compounds (e.g., caffeine and polyphenols). Although these bioactive substances need to be removed for agricultural purposes, they can serve as valuable additives across diverse industrial sectors (e.g., food & beverages, pharmaceuticals, and cosmetics). In pursuit of circular bio-economy, this study investigates a comprehensive valorization approach, (i.e., a rinsing process followed by concentration step via membrane distillation) to enhance SCGs reutilization as soil amendment while simultaneously obtaining a valuable SCGs extract enriched in bio-additives. Specifically, after being collected from a local cafeteria and dried at 25°C, SCGs underwent four rinsing cycles, following the procedure outlined in a previous study [1]. This resulted in two fractions: the rinsed solid SCGs, i.e., the SCGs amendment, and a diluted SCGs extract. Subsequently, the extract was further concentrated through membrane distillation step in a cross-flow lab-scale system using a PTFE commercial membrane (active area of 140 cm²). In this concentration step, the feed and the permeate temperature were kept at 60°C and 25°C, respectively. Evaluation of the process effectiveness and concentrate quality was performed by monitoring caffeine concentration with HPLC-UV/Vis analyses and total polyphenol content (TPC) through Folin-Ciocalteu spectrophotometric assay. Results showed the possibility to reach high concentration factors of up to 8 (equivalent to almost 90% of water recovery), while maintaining high fluxes (above 15-10 L m⁻² h⁻¹). Notably, the concentrate quality was preserved and no transfer of organic matter to the distillate side was observed. On the other hand, SCGs amendment was thoroughly characterized by mixing it with quartz sand at mass ratios ranging from 1% to 20%, revealing decreased bulk density, significantly higher electrical conductivity, enhanced water holding capacity, and a moderate decrease in pH. Additionally, the adsorption capacity of the SCGs amendment was evaluated through both batch tests with copper sulfate solutions of increasing concentrations (125-625 mg/L), and dynamic leaching tests in unsaturated soil-amendment packed columns, showing good affinity for copper sulfate in both scenarios. Finally, absence of caffeine and polyphenols release during leaching tests proved the effective removal of monitored compounds, further attesting to the feasibility of the proposed valorization approach.

Acknowledgments

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

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Supraparticles as a controlled release for fertilizers: synthesis, characterization, and fate in soil columns

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Keywords: supraparticles; nanoparticles; controlled release; sustainable agriculture.

Abstract

Technological advancements in the agricultural sector have increased significantly in recent years to enhance food production. For instance, nano-enabled agrochemicals have emerged as promising tools because they facilitate the controlled release of active ingredients and mitigate environmental impacts [1]. However, concerns about the fate of some nano-enabled materials in the environment have sparked interest in the development of novel materials. Supraparticles (SPs) are self-assembled structures synthesized from primary colloidal particles that can retain the properties of individual nanoparticles, enabling controlled release of agrochemicals with low mobility in soil [2]. Herein, inorganic supraparticles were designed using the evaporation-induced self-assembly method on a superhydrophobic surface, employing Zinc Oxide nanoparticles (ZnO NPs). SPs were characterized using several analytical techniques, and their in vitro release profile was assessed in aqueous media. Additionally, the mobility of SPs were evaluated in soil columns compared to Zinc Sulfate (ZnSO_4) and Zn NPs. Stereoscopic Microscopy analysis showed the evaporation process during the formation of SPs over time. Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) demonstrated spherical morphology and the presence of ZnO NPs inside the SPs. Also, an in vitro release kinetics study of Zinc ions from ZnO SPs revealed a slow-release profile of the nutrient from SPs. Mobility assays of NPs, ZnSO_4 , and SPs in soil columns showed that SPs have reduced nutrient mobility compared to ZnSO_4 and ZnO NPs. Therefore, supraparticles represent an innovative system for delivering agrochemicals and can contribute to developing sustainable agricultural practices.

Acknowledgments

This research was supported by FAPESP (#2022/03219-2, #2023/09217-4 e #2023/00541-3, #2023-12087-5), CNPq (#161360/2021-1), and CAPES (Finance Code 001).

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Unravelling Soil Chemical Changes during Cd Remediation with Lime, Zn and Spent Mushroom Compost (SMC) in Potato-cultivated Soils

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Keywords: Cadmium, remediation, multi-surface modelling.

Abstract

Applications of inorganic or organic amendments to limit crop Cd uptake often show inconsistent results due to the complex chemical changes in several soil properties, which may present synergistic or antagonistic effects on soil Cd immobilization ^[1,2].

A glasshouse pot experiment was set up to study the changes soils and soil solutions underwent throughout the growth season of potato plants under the applications of lime, Zn and SMC (individually or combined). Cd availability was assessed in 1 mM Ca(NO₃)₂ and 0.1 M CaCl₂ extractions, as well as in in-situ collected soil pore water. Other important soil parameters were also monitored, such as pH, soil organic matter, dissolved organic matter and major cations. With an emphasis on soil chemical processes, a mechanistic multi-surface model^[3] was employed to help identify the individual contribution of each soil property to Cd (im)mobilization.

Results indicate that soil pH changes induced by liming had the most pronounced effect on reducing dissolved Cd in all extracts. Increasing doses of SMC increased the most readily available Cd for plant uptake as measured in soil pore water and in 1 mM Ca(NO₃)₂, an intended proxy for soil pore water. However, SMC reduced dissolved Cd measured in the stronger extraction, 0.1 M CaCl₂, most likely by providing more adsorption sites in soils. While Zn is meant to compete with Cd for root adsorption, it also increased dissolved Cd due to competition for adsorption in soils, especially at higher dissolved Cd concentrations. Overtime, plant nitrate uptake led to an increase in pH_{water} by up to 1.2 units as a result of the cation-anion imbalance.

Acknowledgments

This study is part of the CREDIT project (Ref 17S254), funded by the Irish Department of Agriculture, Food and the Marine (DAFM). Yuwei Qin acknowledges the postgraduate scholarship under the same project and the financial, technical and knowledge support from Teagasc and Wageningen University. We gratefully appreciate the assistance received from the farm staff during the greenhouse experiment at Oak Park, Crop Research Centre in Carlow. We also acknowledge the analytical laboratory at Johnstown Castle, Ireland and the soil chemistry laboratory (CBLB) at Wageningen University for their analyses provided.

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Behavior of membrane distillation in the treatment of a diverse range of real and industrial water streams: challenges and future perspectives

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Keywords: Membrane distillation; Industrial wastewaters; Desalination; Fouling; Wetting.

Abstract

In this work, membrane distillation (MD) was challenged with real water and wastewater samples. Specifically, PVDF hydrophobic membrane performance was evaluated with samples derived from a diverse range of sources, including the textile and chemical industry, with the aim of water reuse.

First, water samples were characterized by analysis of the total organic carbon (TOC), pH, electrical conductivity, surface tension, and through ion chromatography measurements. Then, MD tests were carried out with PVDF membranes in a bench-scale system, with the aim of investigating the membrane productivity and rejection, while evaluating the effects of wetting and fouling phenomena.

The feed water characterization showed a diverse organic content, which was high for some of the sources (200-600 ppm), high electrical conductivity (2-50 ms/cm) and low surface tension for some of the sources (30-40 mN/m). Such diversity and compositions allowed investigation of the potential of MD to target an ample range of water streams.

The tests showed a clear development of the wetting phenomenon, highly correlated with the feed water surface tension, confirmed by the continuous increase of the distillate electrical conductivity (used as a proxy for salt passage) and by the sharp decrease of the membrane contact angle that was detected at the end of the tests. The membrane productivity generally showed a moderate decrease during the tests, probably due to the fouling layer that developed over time on the membrane.

The results proved that MD is either unfeasible or requires appropriate feed water pre-treatment for its suitable exploitation. However, high TOC and salt rejection values, together with feasible productivity values, indicated that the PVDF membranes may be suitable for the treatment of a few types feed waters derived from different sources and industries.

Acknowledgments

Funded by the European Union (Grant Agreement #101091915, MEloDIZER, HORIZON-CL4-2022-RESILIENCE-01). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HADEA). Neither the European Union nor the granting authority can be held responsible for them.

Nanofiltration of positively charged caine type local anesthetics from wastewater: performance and selective removal

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Keywords: caine drug; pharmaceutical nanofiltration; wastewater; anesthetics; membrane separation.

Abstract

Natural waters contain a number of substances with high chemical activity (pharmaceuticals, antibiotics, pesticides), which are known to have a wide range of harmful effects, from bacteria to humans, so it is vital to reduce their levels by effectively treating wastewater. In our experiments, we removed 5 local anaesthetics (lidocaine, tetracaine, procaine, benzocaine, bupivacaine) from aqueous solutions using two types of nanofiltration membranes (NF270, NF90). Deionized water, NaCl solution at 10 mM concentration and model wastewater (10 mM ionic strength) were used as background medium. The removal of local anesthetics with the selected membranes can be accomplished to varying degrees. NF270 has a higher permeate flux than NF90 but does not reject some smaller pharmaceuticals (benzocaine, procaine and tetracaine) by more than 80%. NF90 rejects procaine and tetracaine by more than 80% at the expense of a lower permeate flux. Increasing the ionic strength of the filtration media decreased permeate flux and rejection for NF270 and NF90. Using model wastewater for measurements increased the rejection for both membranes and lowered permeate flux for NF270. Steric exclusion played a dominant role for NF90, while for NF270 steric exclusion and Donnan exclusion both played a major role. The effects of divalent ions were twofold: changing the structure of the membrane and increasing the zeta potential. For removing the selected 5 local anesthetics from natural waters NF90 membrane can be a good choice.

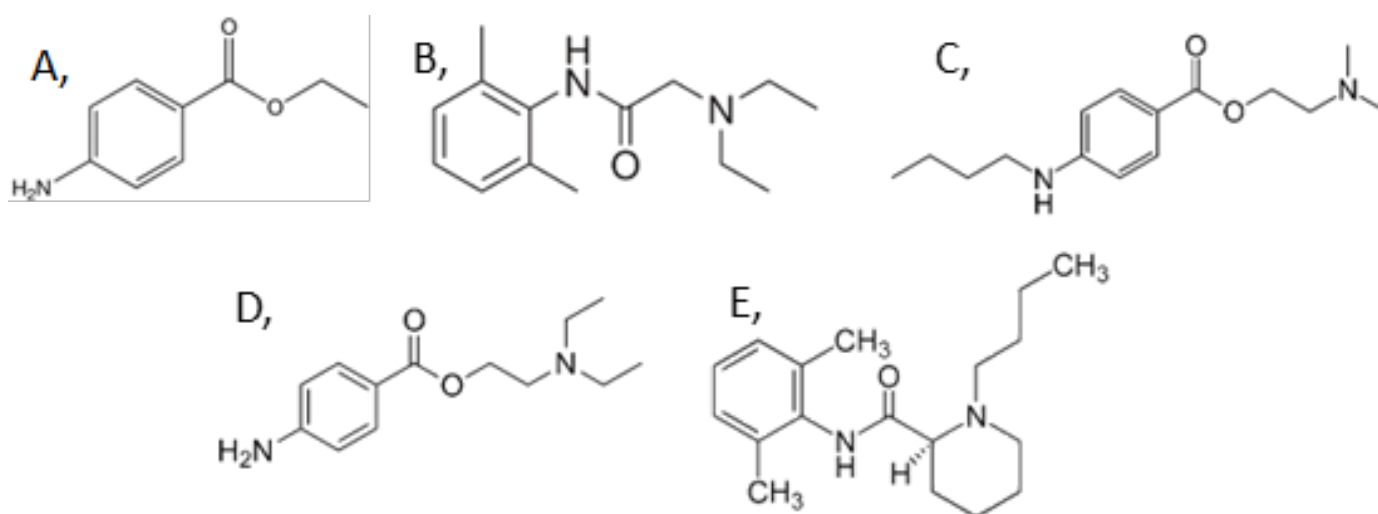


Figure 1: A, Benzocaine, B, lidocaine, C, tetracaine, D, procaine, E, bupivacaine

Enhancing Membrane Distillation for Water Desalination through Distributed Solar Radiation: A Numerical and Experimental Study

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Keywords: Membrane Distillation; Solar Radiation; Numerical Modeling; Experimental Validation; Sustainable Water Treatment

Abstract

Water scarcity and pollution continue to pose significant global challenges, necessitating innovative purification and desalination technologies. This study, conducted at the Department of Energy (DENERG) of the Polytechnic University of Turin, focuses on advancing membrane distillation (MD) for water desalination, leveraging distributed solar radiation as a sustainable and efficient energy source. The core of our research involves the development of a detailed numerical model that simulates the performance of MD systems under various operational conditions, including the integration of solar energy. This model aims to optimize MD processes by enhancing efficiency and scalability, thereby offering a viable solution for treating water with contaminants of emerging concern, such as PFAS. In collaboration with the Department DIATI, we are validating the numerical model against experimental data, emphasizing the model's applicability to real-world scenarios. Preliminary results demonstrate the potential of solar-enhanced MD in achieving high-efficiency desalination, underscored by significant reductions in energy consumption and operational costs. The study not only bridges the gap between theoretical models and practical application but also contributes to the body of knowledge on sustainable water treatment methods. Our findings underscore the importance of interdisciplinary approaches and the integration of renewable energy sources in addressing the pressing issue of water purification. Future work will focus on scaling the technology for pilot-scale implementation and exploring the feasibility of treating various contaminated streams, aiming to contribute to the development of resilient and sustainable water treatment infrastructures.

Assessment of Drinking Water Treatment Processes in Nanoplastics Removal: Pilot- scale and Modelling Studies

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Keywords: Nanoplastics; Drinking water treatment; Ozonation; Sand filtration; Granular activated carbon.

Abstract

Plastic pollution of water bodies is a global environmental concern. Microplastics (diameter between 1 μm and 5 mm) have been already detected in both potable water sources and tap water. Moreover, the environmental degradation of microplastics to produce smaller particles (nanoplastics, particle size $< 1 \mu\text{m}$) has been demonstrated in laboratory experiments, leading to concerns about the efficacy of current drinking water treatment processes to remove these contaminants.

The aim of this study was to investigate the nanoplastics (NPs) removal efficiency through different filtration media typical of drinking water treatment plants (DWTP), i.e. sand and activated carbon. Two pilot-scale filtration experiments of surface water collected from the Lake Zurich were conducted at the Zurich Water Works (WVZ-Lengg, Zurich, Switzerland). The lake water was spiked with NPs and injected in two filters (diameter 1.1 m, length 2.65 m) respectively filled with granular activated carbon and sand. Metal doped NPs (200 nm) were used to track the mobility and retention of these particles within the filter media. Results from the pilot-scale DWTP showed higher retention of NPs in the sand filtration compared to activated carbon.

The MNMs software (Micro- and Nano-particles transport, filtration and clogging Model Suite – www.polito.it/groundwater/software) developed at Politecnico di Torino was used to model the breakthrough curves obtained from the pilot-scale DWTP to derive the hydrodynamic parameters of the filtration systems and characterize the filter retention capacity. The calibrated model was then used to simulate the behaviour of NPs in a full-scale DWTP composed of multiple filtration steps, i.e. rapid sand filtration, activated carbon filtration and slow sand filtration. Modeling results indicate a high capability of the filtration units in DWTPs to remove NPs from water across the entire treatment chain ($>99\%$). According to the results from the model, the removal of NPs during slow sand filtration dominated the overall NPs removal (3.6 log removal). The results of this study can serve as a baseline for assessing the performance of DWTPs to remove NPs from polluted water sources and the capability of current water treatment infrastructure to provide plastic-free, potable water.

Laboratory measurement of saturated soil resistivity to assess the applicability of microbial electro-remediation in contaminated aquifers

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Keywords: groundwater; pollutants; electro-bioremediation; soil; conductivity

Abstract

Groundwater pollution is a global issue due to contaminants like aromatic compounds, chlorinated hydrocarbons, metals, and nutrients from various sources. Developing sustainable technologies to address these complex mixtures is crucial.

Current methods for in-situ remediation of contaminated aquifers are based on subsurface injection of chemicals, such as oxidizing or reducing agents, to induce degradation or transformation of contaminants. However, these approaches have some drawbacks, like difficult subsurface distribution of the chemicals and high costs due to necessity of frequent reinjections. Microbial electro-remediation (MET) offers a sustainable alternative. MET uses electric current to support microbial processes able to degrade pollutants, with no further addition of chemicals. However, the actual applicability of MET process in a contaminated site strongly depends on the resistivity properties of the aquifer.

The electrical conductivity of saturated porous media is described by Archie's Law, an empirical law for the effective conductivity of fully or partially saturated soil. The most important parameters to which it refers are the porosity of the rock ϕ and the pore saturation S_w .

$$C_t = \frac{1}{a} C_w \phi^m S_w^n$$

Among the other factors on which C_t depends we observe the electrical conductivity of the aqueous solution C_w , rock cementation exponents m and saturation n , and the tortuosity a .

In this study, the electrical properties of a sandy soil were characterized to understand the different factors that affect its resistivity and, therefore, the potential applicability of MET approaches. Measurements were performed both in batch conditions and in columns packed with background groundwater flow. Batch measurements were performed by the penetration in the soil of a pair of electrodes that permit to induce both a potential difference and the measurement of resulting current. The characterization was obtained by working with different salt solutions (for example, NaCl, Na₂SO₄, MgCl₂) and different concentrations to evaluate the response of the conductivity to these variables which represent the conditions that a soil can encounter. Measurements in packed columns were performed through a couple of electrodes inserted for the application of voltage and an array of monitoring electrodes distributed along the column for current and potential measurements. Unlike batch analyses, this analysis setup allows the profile of a terrain to be simulated more precisely. Comparison of batch and column results allowed to characterize the porous medium resistivity in different conditions and to highlight the influence of water ionic composition onto the electrical properties of the soil.

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Prediction of cadmium bioavailability in the rice-soil system on a county scale based on the multi-surface speciation model

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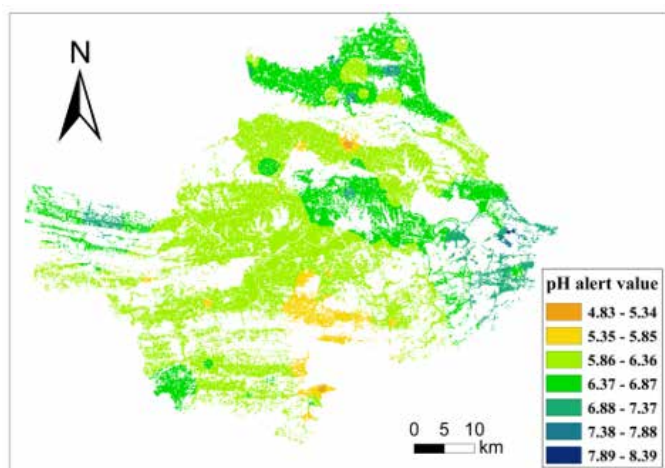
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Keywords: Cadmium; Rice; Bioavailability; Multi-surface speciation model; Precise remediation.

Abstract

Relative to total cadmium (Cd) content, bioavailable Cd in paddy soil is regarded as a more reasonable indicator for the risk of Cd bioaccumulation in rice. However, there is still a lack of approach to accurately predict the content of bioavailable Cd in paddy soil due to its heterogeneity and complexity. Here, multi-surface speciation model (MSM) was employed to predict the bioavailable Cd and Cd immobilization effect. Moreover, a precise remediation strategy was designed based on screening and scenario simulation of the sensitive factors with MSM. The results demonstrated that MSM can well predict Cd bioaccumulation risk in rice. The contribution of pH to Cd bioavailability was quantified under three analysis scenarios, accounting for 87.51% of the total variance of bioavailable Cd. In addition, the pH alert value (6.31 ± 0.52) for Cd risk was acquired for each rice field on a county scale. A precise map for the application amount of lime materials was constructed by taking CaCO_3 ($3.38\text{--}15.75 \text{ t ha}^{-1}$) as a recommended economical and green immobilization agent. This study provides a potentially effective approach for risk assessment of Cd contamination in rice and important reference for precise Cd remediation in paddy soil.



pH alert value mapping

Fig. 1 The distribution of pH alert values based on IDW spatial interpolation with cross validation

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 41877030 and 41977023), the Natural Science Foundation of Hubei Province (No. 2020CFA013).

Synthesis of magnetic beads based on alginate and chitosan for the removal of silver nanoparticles from aqueous solution

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Keywords: polymeric beads; pollution remediation; silver nanoparticles; environmental sustainability.

Abstract

For a long time, the indiscriminate pollution of water bodies due to the disposal of heavy metals and organic compounds has been a global concern. These pollutants have the potential to bioaccumulate in the environment, resulting in toxicity for marine life and posing risks to human health [1]. Moreover, the increasing production and indiscriminate use of inorganic engineered nanoparticles (ENPs) have led to their introduction into the environment, raising concerns about their potential as emerging contaminants. In this regard, with the aim of enhancing environmental remediation processes, various devices have been developed over the last decade [2]. However, few of these address the remediation of inorganic ENPs. Therefore, this study aimed to synthesize polymeric spheres of sodium alginate and chitosan with magnetic nanoparticles using the ionic gelation method and to investigate their capacity to adsorb silver nanoparticles (Ag NPs) in aqueous media. Optical and Scanning Electron Microscopies demonstrated that the magnetic polymeric beads presented a size distribution of ca. 1 μ m, spherical morphology, and high roughness and porosity. Furthermore, the magnetic beads could adsorb more than 80% of the Ag NPs within 3 hours. Additionally, magnetic beads showed excellent recovery capacity in an aqueous medium when submitted to a magnetic field, facilitating their environmental removal. Therefore, these findings play an important role in developing sustainable solutions for the remediation of emerging contaminants (such as inorganic ENPs) in the aquatic environment.

Acknowledgments

FAPESP (#2022/03219-2, #2023/09217-4 e #2023/00541-3), CNPq (#161360/2021-1) and CAPES (finance code 001).

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Potable water recovery from representative aqueous solutions from lunar regolith via direct contact membrane distillation (DCMD)

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Keywords: DCMD; membrane distillation; methanol separation; hydrophobicity; water recovery.

Abstract

Membrane distillation (MD) is conventionally operated through introducing a temperature gradient across a hydrophobic microporous membrane to drive the water vapor from the feed to the distillate sides [1]. Nonetheless, there are few studies on MD process of volatile non-water compounds. Yao et al. [2] investigated the influence of different volatiles on flux. Their study involved distillation of water + ethylene glycol, isopropyl alcohol (IPA), butoxyethanol, and acetic acid. Their results implied the possibility of effective separation of volatiles and water using MD, particularly if there is a significant difference in boiling point and latent energy of evaporation value. Moon rocks (regolith) contain water and other volatiles, and they need to be separated if extraction of high-quality water is the goal of the process. [3]. Therefore, MD can be considered a prospective technology in such an application.

In this study, a lab-scale DCMD device with a PVDF commercial membrane was used to carry out the MD separation of water and volatiles, in synthetic aqueous solutions (see Table below) mimicking those extracted from lunar regolith. To optimize the operating parameters using DoE, for the first 3 feeds, methanol concentration, feed temperature, and distillate temperature were considered as factors with corresponding levels, while the methanol concentration in the feed and distillate were considered as the response for the response surface methodology (RSM) model. While for the 4th feed, a combination of DCMD and oxidization processes were carried out. The chemometric agile tool (CAT) software was used to develop the RSM model and the optimal values were predicted. Finally, additional tests were performed according to the predicted parameters of our model, to validate it and evaluate the potential of MD to perform the sought separation.

Feed no.	Composition	Concentrations
1	DI water + Methanol	Methanol 3 (mg/L)
2	DI water + Methanol	Methanol 30 (mg/L)
3	DI water + Methanol	Methanol 100 (mg/L)
4	DI water + Methanol + IPA + Acetic Acid + Ethylene Glycol + Ethanol + Propylene Glycol	Methanol: 5 (mg/L), IPA: 45 (mg/L), Acetic Acid: 15 (mg/L), Ethylene Glycol: 10 (mg/L), Ethanol: 10 (mg/L), Propylene Glycol: 45 (mg/L)

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Performance Assessment of Filters Developed to Capture Microfibers Released during Laundering with Household Washing Machines

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Keywords: microfibers; household machine; filters; microplastics; laundering.

Abstract

Plastic microfibers, predominantly originating from household laundry activities, such as washing machines, have emerged as a concerning form of pollution in recent decades, requiring urgent management [1]. These microfibers are either conveyed to sewage networks or reach the environment through alternative pathways [2]. Despite typical wastewater treatment plants (WWTPs) achieving elimination efficiencies of up to 90–95% for microfibers and microplastics, approximately 3.68 billion fibers still accumulate in separated sludge, leading to the daily release of approximately 85 million fibers into marine environments [3, 4]. Consequently, several strategies have been developed to intercept these shed microfibers directly at the source, namely, wastewater stream of laundering systems, before they reach aquatic environments, such as in-drum equipment and ex-drum filters [5]. This study investigates the efficiency of commercial microfiber filters from LUV-R, AEG, and *PlanetCare* in terms of microfiber retention when installed inline of a household washing machine. To assess the filter performance, ten washing cycles were conducted, measuring both the captured microfibers and those escaping the filters. A weighing approach was implemented to quantify microfibers by using a Buchner filtration system equipped with a 1.6 μm membrane.

The results indicate that PlanetCare exhibited the highest removal rate standing at $67.5 \pm 3.2\%$, compared to LUV-R ($34.9 \pm 1.6\%$) and AEG ($52.0 \pm 2.5\%$), despite having the largest mesh size of 200 μm compared to 175 μm (LUV-R) and 50 μm (AEG). This difference may be attributed to the embedded foam strips within the PlanetCare filter, playing the role of a secondary filtration. While none of the filters achieved $>90\%$ removal rate, a significant fraction was removed from the wastewater stream. However, the development of new and more efficient filters is imperative to significantly reduce aquatic contamination by plastic microfibers.

Acknowledgments

The study was supported by Politecnico di Torino and the CleanWaterCenter@PoliTo.

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Modeling mass and heat transfer mechanisms occurring across a hydrophobic membrane in Osmotic Membrane Distillation (OMD)

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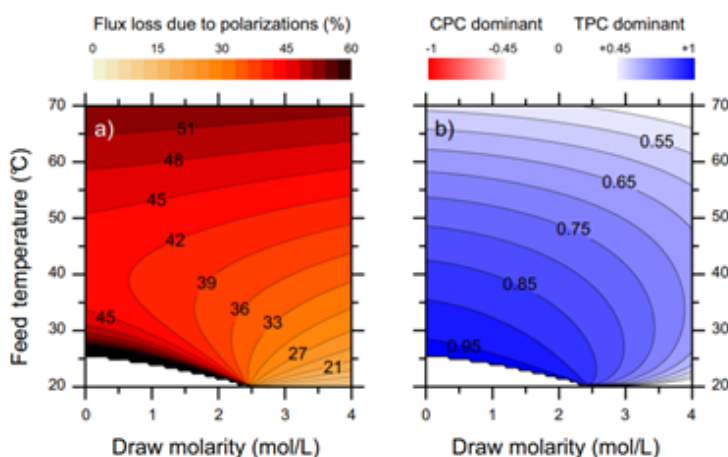
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Abstract

Osmotically-assisted membrane distillation (OMD) may represent an effective technological solution to concentrate valuable non-volatile components from water streams through enhanced interfacial evaporation. In OMD a diluted hot feed stream and a concentrated cold draw solution are separated by a hydrophobic membrane that allows the transport of water vapor from the hot side to the cold side. The driving force of the process is the vapor pressure gradient across the two stream-membrane interfaces.

A comprehensive modeling of the conjugated heat and mass transfer mechanisms occurring across the various interfaces is proposed in this research, including polarization effects at the solid-water interfaces. The developed physical based model combined the Maxwell-Stefan model and dusty-gas model to retrieve the specific interfacial evaporation rate and the consequent latent and conduction heat transfer [1]. To validate the model, the OMD process was also experimentally investigated deploying a lab-scale rig. A key interfacial phenomenon of this process are the temperature and concentration polarization effects – these values near the membrane are different from the corresponding bulk values because of boundary layers formation. The results reported in the Figure below show the productivity losses due to aforementioned polarization effects, and the relative impact of concentration and temperature polarizations on the conjugate polarization. The results were obtained by considering a CaCl₂ aqueous solution at bulk temperature of 20°C as draw agent to concentrate a 4 M LiCl based aqueous solution showing that OMD can be successfully enter the portfolio of interfacial evaporation processes that offer enhanced efficiency, reduced energy consumption, and improved resource recovery.



Considered feed stream: 4 M LiCl-based aqueous solution; panel a) quantify the relative water vapor flux loss due to polarization while panel b) quantify the partial linearized contribution of temperature (i.e., θ_s equal to 1) and concentration (i.e., θ_T equal to 1) polarization phenomena to the full polarization loss.

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Generic CD-MUSIC-eSGC model parameters to predict the surface reactivity of iron (hydr)oxides

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Keywords: iron (hydr)oxides; surface charge; surface complexation model; generic protonation parameters; database

Abstract

The surface reactivity of iron (hydr)oxides plays a crucial role in controlling their interfacial reactions, for which various surface complexation models have been developed. The diversity of mineralogical properties of iron (hydr)oxides has resulted in a redundancy of model parameters, which hampers the modeling of iron (hydr)oxides in soils and sediments, where goethite, hematite and ferrihydrite dominate the iron (hydr)oxide mass fraction.^{1,2} To capture their combined surface reactivity, optimized generic protonation parameters of the Charge Distribution-Multisite Complexation (CD-MUSIC) extended-Stern-Gouy-Chapman (eSGC) model were derived by reanalyzing literature datasets and tested with some newly synthesized iron (hydr)oxides. It was observed that the proton and monovalent ion affinity constants of the different iron (hydr)oxides were located in a narrow range. For the singly- and triply-coordinated hydroxyl sites the obtained generic log(affinity constants) were 8.3 and 11.7 for the protonation reaction and -0.5 for the reaction with the monovalent background ions. Their combination with fixed site densities of singly-/triply-coordinated hydroxyl sites of 3.45/2.70, 5.00/2.50, and 5.80/1.40 sites/nm² for goethite, hematite, and ferrihydrite, respectively, provided good results. The Stern layer capacitances of the inner and outer Stern layers were set equal and could be acquired by an empirical correlation with the sample specific surface area (SSA). The CD-MUSIC-eSGC model with the generic model parameters enables good quality predictions of the proton reactivity of iron (hydr)oxides in 1:1 electrolyte solutions regardless of the sample heterogeneity. The advantages of the generic CD-MUSIC-eSGC model are twofold: (1) protonation of iron (hydr)oxides can be described without making use of spectroscopic measurements and proton titrations, and (2) the model calculations are greatly simplified.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 32061123007 and 41877030) and the Fundamental Research Funds for the Central Universities (No. 2662022ZHQD003).

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Floating Iron Films as a Means for the Transport of Pollutants in an Abandoned Mine Drainage Tunnel in the Harz Mountains, Germany

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Keywords: floating iron films, schwimmeisen; hydrophobic organic pollutants; post-mining.

Abstract

Floating iron films, so called schwimmeisen [1], so far only known to occur naturally in wetlands and estuarine environments [2], were recently observed in an old sedimentation basin in an engine room of a mine drainage tunnel abandoned in 1992. As available research has not assessed whether schwimmeisen plays a role in pollutant distribution, this study investigates if it can act as a carrier for pollutants. The schwimmeisen found here appears to be the result of abiotic [2] and microbiological [3] processes. Since hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAH) and mineral oil hydrocarbons (MOH, e.g. from lubricating oil) are also present in the sedimentation basin, it can be assumed that sorption and formation of coordination and organometallic complexes, likely via template effects and followed by exfoliation processes, play a key role in the formation of these floating iron films. It cannot be discounted that some of this contaminated schwimmeisen will eventually reach surface waters as some flocculents leak out of the sedimentation basin. The floating iron therefore has the potential to mobilise and transport pollutants.

Schwimmeisen and water samples were collected in Feb. 2023 and Feb. 2024. In 2023, the samples were analysed for various organic substances (GC-MS, HPLC-MS/MS). Samples taken in 2024 were investigated for inorganic (ICP-OES, ICP-MS) and organic substances (GC-MS), the mineralogical structure (Mössbauer spectroscopy, DTA, XRD, REM, IR) as well as microorganisms (cell viability, DNA analyses). Analysis of the 2023 samples revealed that the floating iron films were contaminated with a total MOH (C10-C18) concentration of 450 mg/kg and a total PAH (US EPA 16) concentration of 3.7 mg/kg and therefore can not be generally categorized as non-hazardous. Appropriate treatment must be provided prior to any further utilization or disposal. Results for the above mentioned methods will be presented. However, to understand the pollution dynamics of the contaminated floating iron films, further research is required into their structure and composition to be able to ascertain their formation and stability.

Acknowledgments

We would like to thank Mr. Finkeldey (Landesamt für Bergbau, Energie und Geologie of Lower Saxony) for the permission for entry and sampling and Dr. Wilfried Ließmann (TU Clausthal) for the guidance and sharing his expertise on the local geology and mineralogy.

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The effect of combined environmental stressors on *Daphnia magna* and *Brachionus calyciflorus*.

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Keywords: Ecotoxicology; Multi-stressor conditions; Environmental stressors; Acute exposure test.

Abstract

Multiple stressors pose a complex challenge to the environmental health of aquatic ecosystems. Due to climate change and increased anthropogenic influences, ecosystems are exposed to a variety of chemical and non-chemical stressors. However, most ecotoxicological studies focus on single stressors, neglecting the synergistic, additive, or antagonistic effects of multiple stressors. This makes it difficult to identify the main drivers of changes in aquatic ecosystems.

Water quality parameters such as temperature, pH, and salinity are critical for the survival of an organism, and can act as stressors when not present in optimal ranges. The upper and lower tolerance limits for these stressors have been studied individually for the sake of drafting policies and ecotoxicological tests with respect to various model organisms. However, in an ecosystem, these prevailing water quality parameters may be at sub-lethal or lethal levels and may have a synergistic, additive or antagonistic effect on each organism's sensitivity or tolerance towards them. This study delves into the combined effects of temperature, pH, and salinity on two model organisms which are widely used in freshwater ecotoxicological tests, namely *Daphnia magna* and *Brachionus calyciflorus*. The organisms were exposed to pH values of 5, 6, 7, 8, and 9 in combination with salinities of 0.5, 1, 2.5 and 5 PSU at 4 different temperatures- 15°C, 20°C, 25°C and 30°C for an acute test of 48 hr. The mortality was recorded every 12 hr to identify temporal trends. The pH of the exposure media was controlled by the use of zwitterionic Good's buffers. To identify whether such buffers exerted any adverse effects on the test organisms, exposures were also conducted in the suite of EPA synthetic freshwaters which inherently span a range of pH and salinity.

The two organisms exhibited very different sensitivity patterns for the various stressor combinations. Also, there was a drastic effect of pH buffered treatments on the percent mortality of both organisms as compared to the EPA synthetic freshwaters. The study will elucidate how different combinations of non-chemical stressors affect organisms over time during acute exposures and is anticipated to provide valuable insights into ecologically relevant, multi-stressor conditions.

Deposition Behavior of Cellulose Nanocrystal Particles through a Packed Alumina Beads across a Various pH Range

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Keywords: Cellulose nanocrystal (CNC) particles; Packed alumina beads; Charging behavior; Deposition.

Abstract

Investigating transport behaviors of non-spherical nano particles is a crucial issue to decipher the transport of pollutants and nutrients associated with the migration of colloidal particles in soil interstitial water due to non-spherical particles may exhibit significant differences from spherical particles in this regard. This study investigates the effect of pH on the deposition behavior of rod-like cellulose nanocrystal (CNC) particles with surface sulfate groups [1] through a packed alumina beads with three sequential pulse input of CNC particles. Using electrophoretic measurements, we confirmed that the electrophoretic mobilities of CNC particles used in this study do not depend on pH due to their pH-independent surface charged groups. On the other hand, the zeta potentials of the alumina beads' surfaces had been confirmed to vary with pH showing an isoelectric point (IEP) around pH 7 [2].

We further deposition behaviors of the CNC particles with column transport experiments as a function of pH at different NaCl concentrations. We injected CNC suspensions for 20 seconds as a pulse input followed by the background salt solution and quantified the concentration of CNC particles at effluent with a spectrophotometer. We repeated the injection of CNC suspension three times to see the blocking effect.

We observed substantial deposition of CNC particles and blocking at lower pH than isoelectric point (pH~7) due to electrical attraction between negatively charged CNC particles and positively charged alumina beads. At higher pH than IEP, we observed less deposition of CNC particles due to electrical repulsion between CNC particles and negatively charged alumina beads. These results should be analyzed with advection-dispersion equation including deposition and blocking effects to facilitate more quantitative discussions and decipher how the deposition behavior of non-spherical CNC particles differs from the one of spherical particles.

Acknowledgments

This study is financially supported by JSPS KAKENHI (19H03070, 21K14939, 24K17982).

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Molecular characterization of reactive deep underground dissolved organic matters for metal ion using fluorescence spectroscopy and high-resolution mass spectrometry

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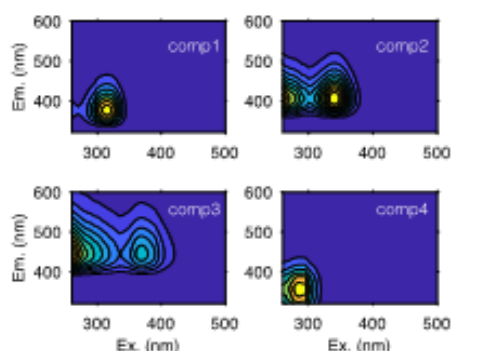
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Keywords: High-resolution mass spectrometry; Radionuclides; Dissolved organic matters; Deep groundwater; Multivariate analysis.

Abstract



Geological disposal is considered to be a feasible option for the final disposal of high-level radioactive wastes. To evaluate the safety of geological disposal, it is necessary to know the reactions of radionuclides with geological media and their migration behaviors in deep underground environments. Among various geochemical reactions that involves dissolved organic matter (DOM), which is ubiquitous in groundwater, can change the charges and sizes of radionuclides by forming complexes, thereby modifying the mobility of radionuclides and their interaction with rock surfaces [1]. In this research, we used Eu^{3+} as a chemical analogue of trivalent actinide elements, and evaluated the molecular characteristics of DOM

components bound to Eu^{3+} by relating the binding properties of DOM and Eu^{3+} obtained by fluorescence spectroscopy to the results of high-resolution mass spectrometry. In fluorescence spectroscopy, quenching experiments with Eu^{3+} were carried out and the different fluorescent components contributing to the binding reaction with Eu^{3+} were extracted, using Parallel Factor Analysis (PARAFAC) [2]. In high-resolution mass spectrometry, mass spectra of DOM in deep groundwater were obtained using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and the chemical formula of organic molecules were assigned to the obtained mass-to-charge ratios. PARAFAC analysis of the EEMs (Emission-Excitation Matrix) from the quenching experiments showed that four fluorescent components can be extracted, each of which binds to Eu^{3+} differently. Among them, comp3, which was suggested to be formed by decomposition of terrestrial organic matters, was revealed to have strong binding ability for Eu^{3+} . By rank correlation analysis between results of PARAFAC of the EEMs and FT-ICR-MS, this component turned out to have low H/C and O/C values and rich in double bonds, and contain a relatively large amount of phytochemicals such as lignin and tannin. Comp1, organic matters of marine origin, was turned out to have weak binding ability for Eu^{3+} , high H/C and O/C, low double bonds, and contain a large amount of lipids.

Acknowledgments

The Ministry of Economy, Trade and Industry of Japan has funded a part of the work as “The project for validating near-field system assessment methodology in geological disposal system” and “Development of the Technology for Integrating Radionuclide Migration Assessments” (2022 and 2023 FY, Grant Number: JPJ007597).

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Passive sampler chitosan/activated carbon for norovirus analysis in water

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Keywords: chitosan; activated carbon; norovirus; passive sampler; adsorption.

Abstract

Human noroviruses are the world's leading cause of acute gastroenteritis in humans. The goal of this study is to design a passive sampler capable of adsorbing sewage and drinking water viruses onto a porous material, then desorbing and quantifying them by genome analysis (RT-qPCR).

Chitosan (CS) and chitosan/mesoporous carbon[1] (CS/CX, X = 10, 50, 100) hydrogel films of controlled thickness (0.5-2 mm) were prepared by spreading acidic solutions of CS or CS/CX (2-3.5% mass. chitosan) and then gelling by soaking in a basic solution. The composition of the CS/CX composite films was varied in the range 20/80 to 50/50 (mass/mass).

While the specific surface area (N_2 , 77K) of mesoporous carbons ranges from 250 m².g⁻¹ to 1540 m².g⁻¹, that of freeze-dried composite films is lower (S_{BET} : 60 - 870 m².g⁻¹) but higher than that of freeze-dried films made from chitosan alone (S_{BET} ~ 7 m².g⁻¹). Scanning electron microscopy (FEG-SEM) of the films showed homogeneous dispersion of the carbon particles and the presence of micro- and macroporosity, confirming the pore size distribution determined by the BJH method (\varnothing_{pore} : ~10-80 nm). Isoelectric point pH values measured by zetametry are around 7 and 4 for the processed films and mesoporous carbons, respectively. Sorption of murine noroviruses ("MNV", a non-human pathogenic virus used as a model for human noroviruses, (\varnothing : ~ 35 nm) were studied in saline water (NaCl 0.1 mol.L⁻¹) and their desorption was studied by varying the physico-chemical parameters of the solution (pH, temperature, time, adsorbent mass, ionic strength, addition of surfactant). MNV adsorption kinetics in saline water (C_0 : 108 ug.mL⁻¹, 10 mg dry material) show that after 2 h contact time, chitosan hydrogel films adsorb ~ 75% of suspended MNVs, while CS/CX composite hydrogel films adsorb up to 98% of MNVs. Under optimal desorption conditions, up to 16% of adsorbed viruses could be recovered. The desorption method gains in performance as the amount of material used during adsorption decreases. The heterogeneity of the material suggests the presence of different adsorption sites, some of which interact strongly with the viruses. The proportion of these sites occupied is lower when the adsorbent/virus ratio is low, which facilitates virus desorption. The porous hydrogel films developed have suitable properties (porosity, surface charge) for the adsorption of MNVs in water. These materials will be tested in real water (water leaving a wastewater treatment plant) to evaluate their potential use as passive samplers.

Acknowledgments

Auvergne-Rhône-Alpes Region (France) for supporting the « VIROCAPTUR » Pack Ambition Recherche Project.

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Carbon materials for the passive sampling of soil gases

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Keywords: passive sampler; mesoporous carbon; VOCs; thermodesorption.

Abstract

Carbon materials selected for the reversibility of their adsorption/desorption properties of volatile organic compounds (VOCs) or semi volatil organic compounds (SVOCs) are currently used as adsorbents for passive sampling of soil gas. These carbon adsorbents are usually introduced in a tube open at one end and placed inside a soil-gas well. In the soil, the passive samplers are used for a given exposure time to collect gases after their diffusion and adsorption. The collected gases are analysed in the laboratory using gas phase chromatography coupled to mass spectrometry after thermal desorption of the adsorbent materials (TD-GC/MS). Passive sampling has the advantage of integrating the concentration levels over a given period of time. However, this type of analysis depends on the nature of the adsorbent, the nature of the trapped compounds and most importantly, the humidity, pressure and temperature conditions inside the soil-gas well.

The aim of this work is to prepare and evaluate various carbonaceous materials for use as adsorbents in passive samplers for soil gas analysis of compounds such as BTEX (benzene, toluene, ethylbenzene and xylenes), polycyclic aromatic hydrocarbons (the more volatile 2- and 3-cycles PAHs, including naphthalene) and halogenated volatile organic compounds (HVOCs: 1,2-dichloroethane, 1,3-dichlorobenzene, etc.).

Carbon materials with mainly mesoporous and macroporous porosity, obtained from different bio-based precursors (chitosan, chitine, glucose) or a synthetic one (phenolic resin), raw or mixed with a commercial carbon black were prepared by pyrolysis or by hydrothermal treatment followed by pyrolysis. Raw and thermally treated commercial carbon black were also investigated. Carbon materials were characterised by N₂ adsorption-desorption (at 77 K) and by scanning electron microscopy (SEM). The adsorption uptake of some VOCs and SVOCs on the synthesised materials was measured in a dynamic mode (breakthrough measurements). Uptake values were compared with those of a commercial adsorbent. In addition, the selected materials with the lowest residual concentrations of emitted VOCs (estimated by thermodesorption) were spiked with a standard solution of VOCs in order to evaluate the VOC thermal desorption properties of these materials. A comparison was then made with the most commonly used commercial adsorbent in passive soil gas samplers.

Acknowledgments

The authors thank the Auvergne-Rhône-Alpes region council for supporting the R&D Booster PREPAG project and IMERYS company for providing carbon black

On the interpretation of the time-response of luminescent bacterial sensors for mechanistic evaluations of metal bioavailability and nanoparticle toxicity in aquatic media

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Keywords: Whole-cell based biosensors; Bioluminescence; Bioavailability; Toxicity; Theory.

Abstract

The exploitation of the bioluminescence signal produced by metal-responsive or stress-responsive lux-based whole cell bacterial sensors is currently restricted to empirical observations and/or consideration of the only maximum signal amplitude over time [1]. In turn, such strategies make it difficult to derive robust quantitative information on metal speciation in solution and on the timescale of cell adaptation/response to a given stress [2]. Based on recent theoretical and experimental work from our group [3-7], this poster details the quantitative connections that can be made between the time-response of metal-detecting luminescent bacterial sensors and the bioavailability of both free and complexed metal species in solution. The theoretical framework derived for the interpretation of data allows the identification of the scenarios where metal biouptake by the sensing cells is rate-limited by metal internalization (as applicable in conventional Biotic Ligand Model or BLM) or metal diffusion from solution, and the cases where metal complexes in solution are inert, dynamic, non-labile or fully labile depending on their contribution to the biouptake flux of free metal species. Quantitative criteria are elaborated for identifying the scenarios where thermodynamic equilibrium speciation models fail and where lability of metal complex and/or bulk metal depletion are relevant. In agreement with experimental data measured for Cd-inducible luxCDABE-based biosensors in the presence of various metal chelators, the formalism successfully predicts/explains the occurrence of shifts of the cell response over time when changing the concentrations of biosensors and/or chelators in solution, - shifts that result from a crosstalk between activation kinetics of cell photoactivity and kinetics of metal depletion from bulk solution. The poster further reports preliminary results on stress-responsive luxCDABE biosensors exposed to manufactured nanodendrimers of medical interest (amine-terminated polyamidoamine dendrimers). The interpretation framework calls here for the consideration of luminometry results together with flow cytometry and confocal microscopy measurements. Overall, our work paves the way for the development of original strategies to exploit the full information-rich response produced over time by bioluminescent biosensors for the assessment of metal bioavailability in solution and the detection/identification of nanoparticles-induced stresses on bacteria.

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