IAP2012

INTERFACES AGAINST POLLUTION

SCIENTIFIC PROGRAM

ABSTRACTS

WWW.iap2012.fr

The 7th International Conference Interfaces Against Pollution (IAP2012), held in Nancy (France) from 11 to 14 June 2012, lies within the framework of a series of conferences initiated in Wageningen (The Netherlands, 1997) and followed in Miskolc (Hungary, 2002), Jülich (Germany, 2004), Granada (Spain, 2006), Kyoto (Japan, 2008) and most recently in Beijing (China, 2010).

As a general objective, IAP conferences seek to provide a forum for researchers working in the interdisciplinary field of Environmental Science. The main focus is brought on the importance of (Bio)Colloids and (Bio)Interfaces in natural media, both from fundamental and applied perspectives. This includes topics of societal concerns like environmental protection, remediation of polluted sites, optimization of mineral resources or the impacts of nanotechnology residues on the environment.

With the course of time, IAP conferences broadened their scope. IAP2012 warmly encouraged the participation of scientists providing that their field of expertise is relevant for the understanding of interfacial processes at model or environmental particles, or that of transfer phenomena in natural sites. In line with the wide spectrum of disciplines (physics, biology, physical-chemistry, chemistry, mineralogy…) relevant for environmental science, IAP2012 is intended to cover research work at the nano-, meso- and macroscopic scales, from transient processes to equilibrium.

The international IAP advisory board and the local IAP2012 organization committees wish that this conference will be an opportunity for researchers who are interested in these increasingly important topics, to shear fruitful discussions in Nancy, a relaxed town from Lorraine, in the eastern part of France.

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Fabien THOMAS and Laurent J. MICHOT, Co-Chairmen.

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SCIENTIFIC AND SOCIAL PROGRAM

Program at a glance

Sunday, June 10

15:00 - 19:00: Welcome and registration – *refreshments from 17:00*

Monday, June 11

7:45 - 8:30: Registration
8:30 - 8:45: Welcoming ceremony
8:45 - 18:00: Scientific sessions
18:00 - 19:00: Informal cocktail party (tasting of wines and local products)

Tuesday, June 12

8:45 - 15h25: Scientific sessions
15:45 - 18:30: Poster sessions
17: 00: Refreshments
19:15: International Advisory Board members meeting/dinner

Wednesday, June 13

8:45 - 17:00: Scientific sessions
18:45: Welcoming drink at the City Hall of Nancy (Place Stanislas)
19:30: Gala dinner in the «Grands Salons» of Nancy City Hall

Thursday, June 14

8:45 - 12h35: Scientific sessions
12:35 - 12:50: Closing ceremony
13:00: Lunch and end of conference

7:45 - 8:30 Registration

Plenary session

WELCOMING CEREMONY (Room Daum)

8:30 - 8:45	D. Waite, President of the International Advisory Board for IAP conferences J.F.L. Duval, IAP2012 Conference Chair

To be continued on page 9

Parallel sessions

SESSION B: RESOURCES AND INTERFACES (Room Daum)

Chair: J. Rose

14:00	KB1	P.M. Biesheuvel	Water desalination using capacitive deionization
14:25	RB1	B. Prélot	On the real performance of solid-solution systems in industrial wastewater treatment: comparison between organic and inorganic ion exchangers
14:45	RB2	M. Barczak	Thiol-functionalized SBA-15 mesoporous silicas as sorbents of platinum (IV) ions
15:05	RB3	M. Bessho	Silica coating on weathered pyrite waste rocks to prevent acid mine drainage

15:45 – 16:05 Coffee break

Chair : P.M. Biesheuvel

16:05	RB4	B. Thiele	Oxidative degradation of sulfonamides by birnessite
16:25	RB5	C. Miller	Visible light-mediated degradation of contaminants by application of Ag@AgCl photocatalysts embedded on reduced graphene oxide
16:45	RB6	Yulun Nie	Efficient inhibition of bromate formation by surface reduction on β-$FeOOH/Al_2O_3$ with ozone
17:05	RB7	Xiaoliang Liang	The effect of transition metal substitution on the catalytic activity of magnetite in heterogeneous fenton reaction: in interface view
17:25	RB8	P. Faure	Degradation of organic pollutants in ancient coking plant soils: reactive minerals effects during air oxidation

18:00 - 19:00 - Informal cocktail party (tasting of wines and local products)

Monday, June 11

Plenary session

SESSION A: SYNCHROTRON SOURCE AS A TOOL IN ENVIRONMENTAL SCIENCE (Room Daum)

Chair : L.J. Michot

08:45	IA1	T. Schäfer	Interfacial processes on colloids and rock surfaces investigated by laser- and synchrotron based spectromicroscopic techniques
09:30	RA1	C. Rivard	Combination of multi-scales and multi-edges X-ray spectroscopies for the investigation of kaolinite and metallic iron interactions
09:50	RA2	D. Waite	Fe(II)-mediated transformation of ferrihydrite to goethite and associated reduction of U(VI) to U(V): thermodynamic and kinetic considerations
10:15	KA1	N. Janot	Speciation of uranium(IV) species in a bioreduced aquifer

10:40 – 10:55 Coffee break

Chair : D. Waite

10:55	RA4	E. Montargès-Pelletier	Distribution and speciation of nickel in hyperaccumulating plants from south africa
11:15	RA5	C. Quantin	Chromium speciation and dynamics in tropical ultramafic soils: a synchrotron based study
11:35	RA6	I. Bihannic	Textural organisation of clay-rich anisotropic porous materials: a neutron scattering study.

11:55 - 14:00 - Lunch

Parallel sessions

SESSION C: INTERFACIAL PROCESSES (Room Gallé)

Chair : M. Avena

14:00	IC1	L.K. Koopal	Humic acids: dissolution and adsorption kinetics
14:45	RC1	Panyue Zhang	Adsorption of methylene blue by humic acid-coated Fe_3o_4 nanoparticles
15:05	RC2	J. Gregory	The interaction between humic acid and aluminium coagulants at different pH values
15:25	RC3	P.E. Reiller	Characterization of humic acid reactivity modifications due to adsorption onto α Al_2O_3

15:45 – 16:05 - Coffee break

Chair : B.L.T. Lau

16:05	KC1	T.H. Nguyen	Transport of biocolloids in a silicon micromodel
16:30	RC4	R. Zimmermann	Design and physicochemical properies of thermo-responsive copolymer films for applications in marine environments
16:50	RC5	E. Lamy	Efect of dual porosity on colloidal transport under saturated and unsaturated flow conditions
17:10	RC6	S. Barany	Flocculation of suspensions by polyelectrolyte mixtures and its use in water treatment
17:30	RC7	Y. Adachi	Initial stage dynamics of flocculation of psl particles induced by an excess addition of polyelectrolytes under high ionic strength

18:00 - 19:00 - Informal cocktail party (tasting of wines and local products)

Tuesday, June 12

Plenary session

SESSION D: ENVIRONMENTAL COLLOIDS AND INTERFACES (Room Daum)

Chair : F. Thomas

08:45 - 09:30	ID1	H.P. Van Leeuwen	Physicochemical dynamics of aquatic nanoparticulate metal complexes

Parallel sessions

SESSION D: ENVIRONMENTAL COLLOIDS AND INTERFACES (Room Daum)

Chair : R. Kretzschmar

09:35	KD1	T. Saito	Size and elemental analyses of nano-colloids in deep granitic groundwater: implications for transport of trace elements
10:00	RD1	A. Fritzsche	Occurence of nano-sized, dispersed ferrihydrite aggregates in soil effluents
10:20	RD2	C. Gantzer	Determination of surface properties of viral particles: a challenge to explain their fate In aquatic media

10:40 – 11:00 - Coffee break

Chair : J.F.L. Duval

11:00	RD3	R. M. Town	Chemodynamics of metal complexation by natural heterogeneous soft colloids
11:20	RD4	J. Rose	Mechanisms of formation and reactivity of imogolite types material
11:40	RD5	G. Francius	Soft biological interfaces: physico-chemical properties investigated by atomic force spectroscopy
12:00	RD6	J. Braunschweig	Colloid generation from ferrihydrite macroaggregates by organic compounds enhances microbial reduction rates

12:30 – 14:00 - Lunch

Chair : T. Saito

14:00	KD2	G. Cuello	Neutron diffraction in earth and environmental sciences
14:25	RD7	H. El Hadri	Colloidal copper mobilisation from vineyard soils by field-flow fractionation
14:45	RD8	T. Polubesova	Dom-affected transformation of contaminants on mineral surfaces
15:05	RD9	Wenfeng Tan	Shape evolution synthesis of α-Fe_2O_3 nanoparticles by ascorbic acid and their catalyzed degradation of methylene blue

15:40 – 16:00 - Coffee break

16:00 - 18:30 - Poster session

17h00 - Refreshments

19:15 - International Advisory Board members meeting/dinner

Tuesday, June 12

Parallel sessions

SESSION E: NANOPARTICLES IN THE ENVIRONMENT (Room Gallé)

Chair : E. Tombacz

09:35	KE1	E. Michel	How can magnetic resonance imaging (MRI) and particulate contrast agents with finely tuned interfacial properties help understanding particle transport in soil.
10:00	RE1	E. Klumpp	Transport and deposition of nanoparticles in (model) soils
10:20	RE2	J. Labille	Transfer of TiO_2 nanoparticles in a sandy porous medium driven by the adsobing natural organic matter

10:40 – 11:00 - Coffee break

Chair : Hong He

11:00	RE3	Lian Wang	Bactericidal activity of Ag/CeO_2 catalysts against *Escherichia coli*
11:20	RE4	C. Hurel	Nanoscale TiO_2 particles: relationship between surface properties and toxicity measurements
11:40	RE5	M. Garaud	Multibiomarker assessment of cerium and titanium dioxide nanoparticles ($NCeO_2$ and $NTiO_2$) sublethal effects on freshwater invertebrates
12:00	RE6	M. Planchon	Interactions between microorganisms and TiO_2 nanoparticles in natural water

12:30 – 14:00 - Lunch

Chair : L.K. Koopal

14:00	RE7	C. Rey-Castro	Relevance of interfacial phenomena for the fate and behaviour of synthetic ZnO nanoparticles in aqueous environments
14:20	RE8	Yongsheng Chen	Aggregation of cerium oxide nanoparticles in aqueous solution
14:40	RE9	E. Tombacz	Adsorption of organic acids on magnetite nanoparticles, pH-dependent colloidal stability and salt tolerance
15:00	RE10	D.J. Lapworth	Characterising nanoparticles in sub-oxic environments
15:20	RA3	R. Kretzschmar	Formation of Cu(0) and CuxS nanoparticles in a contaminated floodplain soil and its influence on Hg dynamics ***(shifted from session A)***

15:40 – 16:00 - Coffee break

16:00 - 18:30 - Poster session

17:00 - Refreshments

19:15 - International Advisory Board members meeting/dinner

Wednesday, June 13

Parallel sessions

SESSION B: RESOURCES AND INTERFACES (Room Daum)

Chair : H.P. van Leeuwen

08:45	KB2	O. Johnson	Exploratory research: low-frequency acoustic energy-enhanced bacterial transport in porous media
09:10	RB9	T. Kone	Numerical and experimental investigation of coupled processes affecting transport of an organic pollutant in biofilm-coated porous media
09:30	RB10	Lin Li	Microbial and chemical characteristics in the removal of landfill odors by an integrated-bioreactor
09:50	RB11	G. Echevarria	Modelling nickel mobility in mining spoils from ultramafic laterites
10:10	RB12	R.A. Kristanti	Sustainable degradation of nitrophenols in the rhizosphere of *Spirodela polyrrhiza* using rhizoaugmentation

10:30 – 10:50 - Coffee break

Chair : A. Dabrowski

10:50	RB13	S.S. Nielsen	Stabilization of arsenic, chromium and copper polluted soil by iron oxide amendment
11:10	RB14	T. Wajima	Removal behavior of phosphate from aqueous solution by calcined paper sludge
11:30	RB15	Hongjie Wang	Effect of calcination on the stability and leachability of arsenic in the arsenic bearing ferric and manganese binary oxide
11:50	RB16	Chengzhi Hu	Copper-cyanide complex removal by a novel dual function polyaluminum chloride
12:10	RB17	H.T.B.M. Petrus	Separation of tennantite from chalcopyrite: atomic force microscopy and UV-vis spectroscopy study

12:30 – 14:00 - Lunch

Chair : E. Klumpp

14:00	RB18	O. Riba	Reactivity and fate of iron and iron/nickel nanoparticles in uranium contaminated water
14:20	RB19	Chih-Chao Wu	Using chlorine dioxide as pre-oxidation combine with low ph coagulation to enhance the removal of natural organic matters.
14:40	RB20	Haibo Wang	Combined uv light and chlorine disinfection of reclaimed water: effects on corrosion and water quality within distribution systems
15:00	RB21	C. Meyer	Development of an in situ remediation technology for btex-contaminated groundwater by the use of iron oxide nanoparticles
15:20	RB22	D.E. Akretche	Electroremediation of drilling muds using facilitating agents

15:40 – 16:00 - Coffee break

Chair : Lin Li

16:00	RB23	Yuxuan Wang	Evaluating china's bc emission inventory using bc to co ratios: integrated analysis of ***in situ*** observations and modeling
16:20	RB24	S.K. Sharma	Microbial approach: an aid to environment regeneration – a case study from india
16:40	RB25	Yafei Wang	Catalytic oxidation of o-xylene over pallidium supported on Co_3O_4 catalyst

18:45 - Welcoming drink at the City Hall of Nancy (Place Stanislas)

19:30 - Gala dinner in the «Grands Salons» of Nancy City Hall

Wednesday, June 13

Parallel sessions

SESSION C: INTERFACIAL PROCESSES (Room Gallé)

Chair : Y. Adachi

08:45	KC2	B.L.T. Lau	Adsorption of metal-based nanoparticles: the importance of surface modification from simple to complex organics
09:10	RC8	J. Krüger	Restructuring of organic coatings upon drying: consequences for the accessibility of sorption sites
09:30	RC9	K. Sasaki	Sorption of borate on calcined products of natural dolomite: effect of calcination temperatures
09:50	RC10	B. Campredon	Modelling As(V) sorption behavior on natural and purified illite
10:10	RC11	M. Hebrant	Reactivity of colloidal suspensions of organically modified silica toward metal ions, kinetics and thermodynamic aspects

10:30 – 10:50 - Coffee break

Chair : S. Barany

10:50	RC12	J. Puy	Impact of ionic strength and resin thickness on metal accumulation in diffusive gradients in thin films (DGT)
11:10	RC13	I. Zelano	Nickel (bio)availability in ultramafic systems from goias, brazil: an overlook of the soil compartments.
11:30	RC14	Qingxin Ma	Heterogeneous reaction of acetic acid on MgO, alpha-Al_2O_3, and $CaCO_3$ and the effect on the hygroscopic behavior of these particles
11:50	RC15	P. Moreau	Interactions between Eu(III), phenolic acids and alumina nanoparticles
12:10	RC16	W. Budianta	Sorption of organics contaminant by clayey soil contaminated with heavy metals

12:30– 14:00 - Lunch

Chair : R. M. Town

14:00	RC17	M. Avena	Competition between glyphosate and phosphate for the surface of goethite. Adsorption and ligand exchange
14:20	RC18	M. Graouer -Bacart	Co-adsorption of enrofloxacin and copper(II) on a chalky soil
14:40	RC19	P. Trens	Highly efficient removal of methyl mercaptan and carbonyl sulfide traces using adsorption and catalysis on zeolites and layered double hydroxides
15:00	RC20	P.P. Remy	Comparative reduction kinetics of both organic and inorganic pollutants by chemically synthesized and biomineralized FeII-FeIII green rusts
15:20	RC21	A. Zegeye	Selectivity and reactivity of hydroxycarbonated green rust during nitrate reduction: effects of pH, phosphate and total iron concentration

15:40 – 16:00 - Coffee break

18:45 - Welcoming drink at the City Hall of Nancy (Place Stanislas)

19:30 - Gala dinner in the «Grands Salons» of Nancy City Hall

Thursday, June 14

Plenary session

SESSION F: ENVIRONMENTAL MICROBIOLOGY (Room Daum)

Chair : R. Briandet

08:45	IF1	S. Pillai	Systems ecotoxicology: from transcriptomics, proteomics and metabolomics to phenomics
09:30	RF1	S. Jomini	Electrostatic interactions between nanoparticles and bacteria: how a simple modification of the ames test revealed mutagenicity of TiO_2 nanoparticles?
09:50	RF2	Ji-Zheng He	New insights into microbial mechanisms of nitrification in acid soils
10:10	RF3	F. Jorand	Control of the routes for microbial formation of the hydroxycarbonate FeII-FeIII (green rust) and magnetite by ionic and nonionic polymers

10:30 – 10:50 - Coffee break

Chair : S. Pillai

10:50	IF2	R. Briandet	Spatial dynamics in biofilms architectures
11:35	RF4	A.G. Guezennec	Treatment of arsenic contaminated mining water using biofilms
11:55	RF5	T. Lescure	Bacterial oxidation of arsenic in polluted soils: role of organic matters
12:15	RF6	M. Etique	Control of the hydroxycarbonated green rust stability, a transitory phase from Fe(II) oxidation by *Azospira oryzae*

Closing ceremony

12:35 - 12:50 J.F.L. Duval, IAP2012 Conference Chair
D. Waite, President of the International Advisory Board for IAP conferences

13:00 - Lunch and end of conference

POSTERS

By name of the presentating author

SESSION A: SYNCHROTRON SOURCE AS A TOOL IN ENVIRONMENTAL SCIENCE

PA1	E. Montarges-Pelletier	Micro-scale investigations of the fate of heavy metals associated to iron-bearing colloids in a highly polluted stream.
PA2	C. Quantin	Speciation and fractionation of nickel in pyrometallurgical by-products: consequences for ultramafic environments

SESSION B: RESOURCES AND INTERFACES

PB1	Rogerio Traballi	Mobile infrastructure in a agricultural production
PB2	Honghai Wu	Decolorization-degradation of the azo dye orange G via heterogeneous fenton reaction by waste zinc bearing magnetite compared with synthesized magnetite
PB3	SM Shafiqul Alam	Does climate change a threat to urban governance in bangladesh? An overview on dhaka mega-city
PB4	M.T. Ammami	Enhanced electrokinetic remediation of heavy metals and pahs from dredged marine sediment
PB5	S. Ansanay-Alex	Adsorption of pesticide and pharmaceutical compounds on natural porous minerals
PB6	S. J.Bash Al-Malikey	Effect of filling media on the performance of trickling filters used For the treatment of municipal waste water
PB7	L.S.Belaroui	Study of methylen blue adsorption on the algerian palygorskite
PB8	J.L. Bersillon	Choice of an adsorbent for glyphosate immobilization and biodegradation – physical chemical properties
PB9	A.B. Bigalyev	Determining level of damaged ecosystems of caspean sea area
PB10	L. Bouabdalaoui	Fe/P/S interface as anode in microbial fuel cell for the treatment of wastewater
PB11	L. S. Coulibaly	Adsorption of phosphate by laterite and sandstone from ivory coast: absorbent dose effect and kinetic
PB12	Dąbrowski A	Ordered mesoporous organosilicas as sorbents of heavy metal ions
PB13	M.C. Dictor	Efficiency of arsenic oxidizing bacterial biofilms for arsenic contaminated drinking water treatment
PB14	A.Djafer	Biosorption of Cr(VI) by yeast supported on granular pouzzolan in fixed-bed reactor
PB15	Dong Liu	Preparation of hierarchically porous carbon with high adsorption capability by using diatomite as template and catalyst
PB16	M. Duc	The civil engineering use of methylene blue dye adsorption on fine mineral particles
PB17	Fathi Elosta	Simulation geological environmental shortage water of groundwater and the possibility of activity earthquake Jafarah basin NW Libya
PB18	A. Eswayah	An investigation into heavy metal removal from contaminated sediments using soil washing
PB19	P. Faure	Remediation of pah-contaminated soils by magnetite catalyzed fenton-like oxidation
PB20	S. Semrany	Degradation of carbamazepine by trametes versicolor strain grown on various organic supplements
PB21	L. Filippov	Synergistic effects in mixed collector systems: hf-free flotation method for separation of feldspars ore
PB22	L. Filippov	Reducing of CO_2 emission by carbonation of saline waste solution
PB23	A. Halajnia	The removal characteristics of nitrate and phosphate by Mg-Al-LDHs
PB24	L. Hassenboehler	Activated sludge behavior in the presence of household micropollutants

SESSION B: RESOURCES AND INTERFACES

PB25	C. Magnenet	Functionalization of organic membranes by polyelectrolyte multilayer assemblies. Application to the decontamination of aqueous solutions
PB26	G. Mamytbekov	Colloidal-chemical aspects of in-situ leaching of uranium
PB27	A. Mefti	Reducing power and carbon footprint of the Boumerdes wastewater treatment plant
PB28	A. Mohamadou	Synthesis of task specific ionic liquids for the metal extraction
PB29	W. Oueslati	Relation between hydrous strain and the cationic exchange process in the case of Na-rich montmorillonite : quantitative xrd description
PB30	S. Peulon	Degradation of indigo carmine solutions by thin films of birnessite electrodeposited.
PB31	J. P. Pinheiro	Characterization of low dispersity anionic multi-responsive core-shell polymer particles
PB32	P. Piriou	Effect of chloride salts on the mean bubble diameter in a flotation column
PB33	B. Prelot	Effect of cation competition on strontium uptake by type 4A zeolite from multi-component aqueous solutions
PB34	J.A. Rodríguez-Liébana	Variation in inorganic and organic soil solution composition induced by incubation of an acid soil with organic wastes
PB35	A. V. Sineva	Water purification from surfactants by natural adsorbents
PB36	R. Traballi	Mobile infrastructure in a agricultural production
PB37	R. Traballi	Best number of sample: soil fertilized with sewage sludge
PB38	T. Woignier	Effect of the fractal microstructure of clay on the sequestration of a pollutant in soils
PB39	Peng Yuan	The adsorption of Cu(II) cations by the surface-silylated diatomite (diatomaceous earth) and the effects of heating on the surface silylation

SESSION C: INTERFACIAL PROCESSES

PC1	J. Arfaoui	Comparative study of the promotional effect of second metal (V, Mo, W or Ce) for the low temperature SCR of NO_x with NH_3 over derived sol gel modified TiO_2
PC2	J. Cieśla	Acid and alkali effect on surface properties of soils and their mineral constituents
PC3	D.M. Prieto	Evaluation of phosphorous adsorption and desorption capacity of episammic biofilms developed on streambed sediments
PC4	X.M. Dou	Remediating fluoride from water using hydrous zirconium oxide
PC5	J.F.L. Duval	Electrolyte interface : challenging macroscopic approaches for ion specificity issues
PC6	Hongjie Wang	Adsorption of Cu(II) by aminopropyl-functionalized mesoporous δ-MnO_2 from aqueous solution
PC7	N. Janot	Influence of solution parameters on europium(III), α-Al_2O_3 and humic acid interactions
PC8	M. Kobayashi	Coagulation and charging of latex particles in the presence of natural clay nanotube imogolite
PC9	J. K. Lee	Effects of geochemical conditions on the sorption of uranium, neptunium, and americium by gratite
PC10	C. Liu	Heterogeneous reaction of NO_2 on TiO_2: effect of crystalline phase on surface species
PC11	N. Marmier	Behavior of carbon-14 in cementitious materials
PC12	J. A. Mbey	The role of the starch matrix-kaolinite filler interface in composite biopolymer films
PC13	T. Missana	Modelling of Se(IV) sorption on titanium oxide colloids and effects of sorption on colloid stability
PC14	T. Missana	Adsorption processes in heterogeneous rock: top-down *vs* bottom up approach in modelling experimental data.
PC15	T. Missana	Micro-scale study of uranium retention on granite
PC16	I.Mnif	Behavior of polyacrylamide flocculants and acrylamide in model clays and soils
PC17	S. Mongin	Speciation of cadmium using dgt sensors in quasi-equilibrium conditions
PC18	M.N. Pons	Image analysis applied to long-term monitoring of biofilms
PC19	B. Prelot	Competitive sorption involved in wasterwater treatment: contribution of titration calorimetry to the understanding of competitive mechanisms

SESSION C: INTERFACIAL PROCESSES

PC20	B. Prelot	Correlation between surface energy and hydration properties of montmorillonite saturated with heavy metals
PC21	J.A. Rodríguez -Liébana	Increased sorption of two pesticides on a soil from a mining area added with sewage sludge
PC22	H. Tamon	Synthesis of high-strength zeolite monolith by steam-assisted crystallization
PC23	L. Temdrara	The modification effects on the pore structure properties of activated carbon for the adsorption of phenol
PC24	M.Terashima	Modification of the generic nica-donnan model parameter for the modeling of Eu bindings by deep groundwater humic substances
PC25	H. Wang	Electrochemical reduction of CO_2 to organic acid by a PD/MWNTS gas-diffusion electrode in aqueous medium
PC26	C. Yang	Tylosin sorption and thermodynamics on minerals

SESSION D: ENVIRONMENTAL COLLOIDS AND INTERFACES

PD1	C. Dika	Impact of genome on aggregation and electrokinetics of MS2 phage, influence of the virus purification protocol
PD2	C. Jiang	Investigation of topsoil water dispersible colloids (WDC) release kinetics in batch experiments
PD3	J. Martin	Electrohydrodynamics of multiresponsive core-shell polymer particles
PD4	T. Missana	Analysis of colloid retention in crystalline rock
PD5	E. Montargès -Pelletier	Sorption of metals onto river suspended materials
PD6	H. Morisaki	Biofilm inside environment preventing outside pollution
PD7	Mutaliyeva B.Zh	Colloid-chemical properties of compositions of polyacrilonitrile derivatives with surfactants
PD8	Narkiewicz-Michałek	Studies of propyl gallate antioxidative activity in the n-oxide surfactant solutions
PD9	W. Oueslati	Effect of an applied strain caused by alkaline perturbation on the cationic exchange capacity of dioctahedral smectite: quantitative XRD investigation.
PD10	W. Oueslati	Hydration-dehydration performance of (Na^+, Cs^+) exchanged smectite: effect of the charge location and the cation nature
PD11	S. Peulon	Degradation of glyphosate and AMPA (amino methyl phosphonic acid) solutions by thin films of birnessite electrodeposited.
PD12	Elise Rotureau	Dynamic speciation analysis of metal binding by heterogeneous particles: case of clay minerals
PD13	W. Rudziński	Structural-adsorption characteristics of SBA-15 organosilicas functionalized with different groups
PD14	M. Szymula	Electrochemical studies of alkyl gallates behaviour in SDS/water/EtOH solutions
PD15	Y. Tsujimoto	Rheological behavior of imogolite suspensions

SESSION E: NANOPARTICLES IN THE ENVIRONMENT

PE1	I. Sameut Bouhaik	Aggregation of TiO_2 nanoparticles in aqueous solution: modelling and comparison with experimental data

SESSION F: ENVIRONMENTAL MICROBIOLOGY

PF1	E.S. Hartikainen	Growth and extracellular enzyme production of fungi on cadmium, chromium, cobalt, lithium and manganese containing culture media
PF2	L. Li	Microenvironment characteristic and microbial community in activated sludge flocs of different particle size
PF3	L. Li	SEM/EDX monitoring the biaerosol particles collected by Andersen sampler in a wastewater treatment plant

ABSTRACTS

For each session, abstracts are presented following the time schedule, for oral contributions, and by alphabetical order of the presenting author for posters.

SESSION A:

Synchrotron source as a tool in environmental science: case studies.

IA1

INTERFACIAL PROCESSES ON COLLOIDS AND ROCK SURFACES INVESTIGATED BY LASER- AND SYNCHROTRON BASED SPECTROMICROSCOPIC TECHNIQUES

Schäfer T.,[1,2]* Huber F.,[1,2] Claret F.,[3] Darbha G.K.,[1] Chagneau A. ,[1,2] Jacobsen C.[4]

[1] Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany
[2] Dep. of Earth Sciences, Inst. of Geological Sciences, Freie Universität Berlin, Germany
[3] BRGM, 3 Avenue Claude-Guillemin, BP 36009, Orléans Cedex 2, France
[4] Argonne National Laboratory, Argonne, IL, USA

thorsten.schaefer@kit.edu

Transport of pollutants can occur in the aqueous phase or for strongly sorbing pollutants associated on mobile solid phases spanning the range from a couple of nanometers up to approx. ~1µm; usually called colloids or nanoparticles [1,2]. A new form of pollutants are engineered nanoparticles (ENP's), where properties differ substantially from those of bulk materials of the same composition and cannot be scaled by simple surface area corrections. Potential harmful interactions with biological systems and the environment are a new field of research [3]. A challenge with respect to understand and predict the contaminant mobility is the contaminant speciation, the aquifer surface interaction and the mobility of nanoparticles. Especially for colloid/nanoparticle associated contaminant transport the metal sorption reversibility is a key element for long-term mobility prediction. The spatial resolution needed is clearly demanding for nanoscopic techniques benefiting from the new technical developments in the laser and synchrotron community [4]. Furthermore, high energy resolution is needed to either resolve different chemical species or the oxidation state of redox sensitive elements. In the context of successful planning of remediation strategies for contaminated sites this chemical information is categorically needed. In addition, chemical sensitivity as well as post processing methods extracting trace chemical information from a complex geo-matrix are required. The presentation will give examples of homogeneous and heterogeneous secondary phase formation changing the surface roughness of aquifer material, the speciation of radionuclides through incorporation in these newly formed phases [5], the changes of surface roughness and colloid attachment via mineral dissolution/precipitation reactions [6] and the sorption of humic substances on mineral surfaces leading to functional group fractionation and consequently different metal binding environment as unraveled by time resolved laser fluorescence measurements [7]. Furthermore, aquifer flow path heterogeneity is driving the mobility/retention of colloids/nanoparticles, which can be resolved by tomographic (CT) methods [8]. Reactive transport models use usually simplified geometrical assumptions which are essential to properly predict pore clogging. Here, implementation of 3D µCT information will overcome these shortcomings. Examples of contaminant transport up-scaling from laboratory scale (µmdm) to field scale experiments in underground research laboratories (URL's) will be discussed and based inter alia on the examples given current challenges and potential new directions will be highlighted in the outlook of the presentation.

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[5] K. Holliday, A. Chagneau, F. Claret, T. Schäfer, T. Stumpf Dalton Transactions 2012, 41, (13).
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[7] F. Claret, T. Schäfer, J. Brevet, P.E. Reiller Environ. Sci. Technol. 2008, 42, 8809.
[8] F. Huber, F. Enzmann, A. Wenka, M. Dentz, T. Schäfer J. Contam. Hydrol. 2012, 133, (0), 40-52.

Session A: Synchrotron source as a tool in environmental science

RA1

COMBINATION OF MULTI-SCALES AND MULTI-EDGES X-RAY SPECTROSCOPIES FOR THE INVESTIGATION OF KAOLINITE AND METALLIC IRON INTERACTIONS

Rivard C.,[1,2]* Montargès-Pelletier E.,[1,2] Bihannic I.,[1,2] Vantelon D.,[3] Pelletier M.,[1,2] Michot L.J.,[1,2]
Villiéras F.,[1,2] Michau N.[4]

[1]Université de Lorraine, LEM, UMR 7569, Vandoeuvre-lès-Nancy, F-54500, France.
[2] CNRS, Laboratoire Environnement et Minéralurgie, UMR 7569, Vandoeuvre-lès-Nancy, F-54500, France.
[3] Synchrotron Soleil, Gif-sur-Yvette, F-91192, France.
[4] ANDRA, Châtenay-Malabry, F-92298, France.

rivard.camille@gmail.com

In the context of the geological disposal of high-level radioactive waste, it is of prime importance to understand the interaction mechanisms between the geological matrix and the iron waste package overpack. In order to evidence the individual role of each clay component entering in the mineralogy of the Callovo-Oxfordian clay rock, batch experiments were conducted using pure clay phases (smectite, illite and kaolinite) mixed with metallic iron in conditions close to those of the underground disposal: 90°C and anoxic atmosphere (Rivard [1]).
As far as kaolinite-metallic iron interactions are concerned, classical characterization methods evidence a partial oxidation of metallic iron and a moderate destabilization of the kaolinite associated to the formation of a Fe-serpentine species, berthierine (Rivard *et al.* [2]). To precise the structure of this neoformed phase, synchrotron-based spectroscopic investigations were performed at Si, Al and Fe edges at bulk, micrometric and nanometric scales (Lucia beamline on Soleil Synchrotron and beamline ID10^{-1} at the Canadian Light Source).
XANES and EXAFS analyses reveal that iron is mainly ferrous, octahedrally coordinated and clustered with changes in status from one particle to another. Silicon spectra is slightly affected and still close to the signal of initial kaolinite, which suggests that kaolinite platelets remain present, even for high iron contents. Investigations at Al K-edge evidence the presence of tetrahedrally coordinated aluminum and variations of Al^{IV}/Al^{VI} ratio at both aggregate and particle scales. Whatever the investigation scale, particles appear to be constituted of kaolinite and berthierine layers. By combining spatially-resolved spectroscopic analyses and TEMEDXS elemental distribution, it is then possible to calculate unit cell formulae for the neoformed Fe-serpentines layers as well as abundance of each species in mixed particles. For most investigated particles, results reveal that the variations of particles composition are directly linked to the relative contributions of kaolinite and berthierine in mixed particles. However, for some of them, microscale investigations evidence the crystallization of two other end-members of the Fe-serpentines serie devoid of aluminum: cronstedtite and greenalite.

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[2] C. Rivard, M. Pelletier, N. Michau, A. Razafitianamaharavo, I. Bihannic, M. Abdelmoula, J. Ghanbaja, F. Villiéras Submitted to Am Miner.

RA2

FE(II)-MEDIATED TRANSFORMATION OF FERRIHYDRITE TO GOETHITE AND ASSOCIATED REDUCTION OF U(VI) TO U(V): THERMODYNAMIC AND KINETIC CONSIDERATIONS

Waite T. David, Boland D. and Collins R.N.

School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

d.waite@unsw.edu.au

Results by both our own group and others suggest that the Fe(II)-mediated transformation of ferrihydrite to more crystalline forms such as goethite is critical to the reduction of adsorbed or incorporated U(VI) to U(V) or U(IV) species (e.g., Boland *et al.*, 2011). More recent (as yet unpublished) findings using a novel quick-XAFS method to follow iron oxide transformation and XANES spectroscopy to determine uranium redox state confirm that the rate of reduction of U(VI) to U(V) is similar to the rate of transformation of ferrihydrite to goethite with the rate of iron oxide transformation determined by the extent of adsorption of Fe(II) to the ferrihydrite surface. These results will be presented and used as the basis for analysis of thermodynamic and
Kinetic aspects of the transformation of iron oxides and associated uranium species. The key reactions of Fe(II) adsorption, electron transfer and atom exchange will be discussed with the status of these reactions fundamental to establishment of the local redox potential– the critical determinant of U(VI) reduction.

Boland, D.D., Collins, R.N., Payne, T.E. and Waite, T.D. (2011). Effect of Fe(III) oxide transformation on the Fe(II)-mediated reduction of U(VI). Environ. Sci. Technol. 45(4), 1327–1333.

RA3

FORMATION OF Cu(0) AND CuxS NANOPARTICLES IN A CONTAMINATED FLOODPLAIN SOIL AND ITS INFLUENCE ON Hg DYNAMICS

Kretzschmar R.,[1]* Hofacker A.,[1] Weber F.-A.,[2] Kaegi R.,[3] Voegelin A.[4]

[1] Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, CHN F23.1, Universitaetstrasse 16, Zurich, CH, 8092, Switzerland.
[2] Eawag, Swiss Federal Institute of Aquatic Science and Technology, Duebendorf, 8600, Switzerland

kretzschmar@env.ethz.ch

Riparian floodplain soils are frequently contaminated with a variety of trace metals resulting from decades to centuries of emissions from mining, municipal waste water, or industry. These soils are typically affected by redox fluctuations induced by periodic flooding and drainage, which can occur in different seasons of the year. To investigate the temperature-dependent dynamics of trace metal release to pore water induced by soil flooding, we conducted soil microcosm experiments at 5, 14, and 23°C using a contaminated soil from the Mulde River, Germany [1,2]. Pore water sampled during 33 days of flooding was analyzed for dissolved (<0.025 µm) and colloidal metal concentrations, SO42-, DOC, pH, and Eh, respectively. Colloids were characterized by transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS) at the Cu-K and Hg-LIII edges, respectively. TEM and XAS revealed rapid formation of metallic Cu(0) nanoparticles upon flooding [1]. Hg(0) was also formed and incorporated into the crystal lattice of metallic Cu(0). With onset of sulfate reduction, Cu(0) particles were transformed to CuxS. TEM results suggested that Hg was then incorporated into Cu-rich metal sulfides either as mixed sulfide or as a separate HgS phase. Our new results suggest that the reduction of Cu(II) to Cu(0) and the subsequent transformation to metal sulfides [2] are strongly temperature dependent and that these microbiallydriven processes may have important implications for the dynamics of Hg in soils with mixed metal contamination.

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Session A: Synchrotron source as a tool in environmental science

KA1

SPECIATION OF URANIUM(IV) SPECIES IN A BIOREDUCED AQUIFER

Janot N.[1]*, Bargar J.R.[1], Lezama-Pacheco J.[1], Stubbs J.E.[2], Williams K. H.[3], Long P.E.[3], Suvorova E.[4], Stylo M.[4],Alessi D.[4], Bernier-Latmani R.[4], Campbell K.[5], Davis J.A.[3], Fox P.[3], Cerrato J.M.[6], and Giammar D.E.[6]

[1] Stanford Synchrotron Radiation Lightsource, Menlo Park, CA, USA
[2] University of Chicago, Chicago, IL, USA
[3] Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[4] École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
[5] US Geological Survey, Boulder, CO, USA
[6] Washington University, St. Louis, MO, USA

njanot@slac.stanford.edu

Uranium contamination of groundwater is a concern at several US Department of Energy sites, such Old Rifle, CO. Uranium transport in the environment is mainly controlled by its oxidation state, oxidized U(VI) being highly soluble, and then mobile, whereas reduced U(IV) precipitates easily. Bioremediation techniques of contaminated aquifers aim at immobilizing uranium in a reduced form. Previous laboratory and field studies have shown that the addition of an electron donor (lactate, acetate, ethanol) to the groundwater stimulates the activity of metal-reducing bacteria, which promotes U(VI) reduction in contaminated aquifers. Obtaining information on chemical and physical forms of U(IV) species for sediments biostimulated in the field is challenging due to the low concentration of uranium in the aquifers (typically < 10 ppm). An in-situ technique has been developed for studying uranium reduction dynamics during such bioremediation episodes. This technique uses in-well columns to obtain direct access to chemical and physical forms of U(IV) produced, evolving microbial communities, and trace and major ion groundwater constituents.

The aim of this work was to assess the formation of U(IV) during the early stages of a bio-remediation experiment, in Fe-reducing conditions, at the Old Rifle site, CO. Several in-well chromatographic columns packed with sediment were deployed and were sampled at different days. X-ray absorption spectroscopy and Xray microscopy were used to obtain information on Fe and U speciation and distribution. Chemical extractions of the reduced sediments have also been performed to study the rate of Fe(II) and U(IV) accumulation.

RA4

DISTRIBUTION AND SPECIATION OF NICKEL IN HYPERACCUMULATING PLANTS FROM SOUTH AFRICA

Montargès-Pelletier E.[1]*, Mesjasz-Przybylowicz J.[2], Echevarria G.[3], Briois V.[4], Barnabas A.[2], Sechogela P. [2], Groeber S.[3] and Przybylowicz W. [2,5]

[1]Laboratoire Environnement et Minéralurgie, CNRS Université de Lorraine, F- 54500 Vandoeuvre les Nancy, France
[2]Materials Research Department, iThemba LABS, Somerset West 7129, South Africa
[3]Laboratoire Sols et Environnement, INRA Université de Lorraine, F- 54505 Vandoeuvre les Nancy cedex, France
[4]SOLEIL, SAMBA beamline, l'Orme des Merisiers, Saint Aubin, 91192 Gif sur Yvette cedex, France
[5]on leave from the Faculty of Physics and Applied Computer Science, University of Science & Technology, Krakow, Poland

emmanuelle.montarges@univ-lorraine.fr

Hyperaccumulation is an unusual plant response to soils enriched with heavy metals such as Ni, Co, Zn, and Cd. However, about 2% of plants inhabiting these soils take up and accumulate large quantities of heavy metals in their shoots: a phenomenon known as hyperaccumulation. It has been reported for more than 450 species, mainly Ni accumulating species (about 400) [1,2]. In order to better understand the physiological processes lying behind hyperaccumulation, microanalyses were performed, involving two hyperaccumulating plant species, collected in their native habitat

Two South African Ni-hyperaccumulating plants from the *Asteraceae: Berkheya coddii* Roessler and *Senecio coronatus* (Thunb.) Harv. were collected on ultramafic soils in the Barberton area (Mpumalanga Province, South Africa). Plant samples were cryo-fixed in liquid propane and freeze-dried. Microanalyses of elemental concentration and distribution were performed using particle induced X-ray emission (PIXE, nuclear microprobe at iThemba LABS, South Africa). Spatially resolved X-ray absorption experiments were performed on SAMBA beamline to investigate nickel distribution and speciation within cross-sections of leaves, stems and roots. Incident X-ray beam was reduced in size using a pinhole for a first series of experiments, and using a monocapillary for a second series of experiments. Regions of interest were selected within the different plant tissues by direct visualisation, with the support of elemental profiles and maps acquired by X-ray fluorescence. XAS spectra were then collected at Ni K-edge, at room temperature.

The results show that Ni is predominantly complexed by weak or middle-strong organic ligands, through the presence of carboxylate groups in the first sphere of coordination. Chelation could be definitely excluded from major accumulation mechanism. Spectroscopic signals strongly support the predominance of citrate and malate, low molecular weight ligands, for nickel transport and storage in the hyperaccumulators *S. coronatus* and *B. coddii*, growing in their natural environment.

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[2] E. Maestri, M. Marmiroli, G. Visioli, N. Marmiroli, Envir. & Experim. Bot. 2010, 68, 1.

RA5

CHROMIUM SPECIATION AND DYNAMICS IN TROPICAL ULTRAMAFIC SOILS: A SYNCHROTRON BASED STUDY

Quantin C., [1]*, Garnier J., [2], Montargès-Pelletier E., [3], Vantelon D., [4], Guimaraes E. M., [2], Becquer T.[5]

[1] UMR 8148 IDES, UPS11-CNRS, Bât. 504, 91405 Orsay Cedex, France
[2] Instituto de Geociências, Universidade de Brasilia, CEP 70910-900 Brasília – DF, Brazil
[3] UMR 7569 LEM, CNRS-INPL, 54501 Vandoeuvre-lès-Nancy Cedex, France
[4] Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, 91192 Gif sur Yvette Cedex, France
[5] UMR 210 Eco&Sols, IRD-INRA-SupAgro, 34060 Montpellier Cedex 2, France

cecile.quantin@u-psud.fr

Ferralsols developped from ultramafic rocks in the massif of Niquelândia (Brazil) are extremely rich in Fe (271 to 513 g kg^{-1}) but also in "trace"metals like Ni and Cr. Despite high chromium concentrations in ultramafic soils (6,135 to 9,270 mg kg^{-1}), Cr availability is generally low, as Cr-bearing minerals are considered stable in supergene conditions. However, KH_2PO_4 extractions associated to isotopic exchange kinetics have shown a high Cr(VI) availability in Ferralsols developed on the ultramafic massif of Niquelândia (Brazil) [1].

A study combining mineralogical, geochemical, µSXRF and XANES approaches was performed to assess the solid speciation of Cr and to understand its geneses. Chromium is mostly present in the trivalent form and is included in chromites and Fe-oxides. Nevertheless, a large amount of hexavalent chromium is associated with the clay-sized fraction in the mineral horizons. Mn-oxides, the only natural Cr(III) oxidants, are also present in these horizons.

Microscale investigations revealed the close association of Cr(VI) with Mn-oxides and strongly suggest that Mn-oxides can oxidize Cr(III) into Cr(VI). The XANES analyses show the occurrence of Cr(VI), which is completely removed by KH_2PO_4 extraction, demonstrating that the Cr(VI) is completely sorbed onto the soil matrix, i.e., Fe-oxides.

Finally, the high mobility of Cr(VI), associated with the finest Fe-oxide particles mobilized during runoff following rainy events, may have harmful environmental consequences.

This approach of combining direct and indirect observations allows us to characterize the total extractable Cr(VI) pool of these soils and to give key information on its mobility and localization.

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RA6

TEXTURAL ORGANISATION OF CLAY-RICH ANISOTROPIC POROUS MATERIALS: A NEUTRON SCATTERING STUDY.

Bihannic I.,[1],* Rivard C.,[1] Pelletier M., [1] Michot L.J., [1] Hubert F., [2] Ferrage E., [2] Villiéras F.[1]

[1] Laboratoire Environnement et Minéralurgie, CNRS-Université de Lorraine, UMR 7569, BP40,
15 avenue du Charmois, F-54501 Vandoeuvre-lès-Nancy Cedex
[2] HydrASA, CNRS-Université de Poitiers, UMR 6269, rue Albert Turpain, F-86022 Poitiers Cedex

isabelle.bihannic@univ-lorraine.fr

Argillaceous rocks are weakly permeable porous media with an extremely complex network of pores extending from nanometric to millimetric length scales. These materials display two specific features adding to their complexity: (i) their structure evolves under the action of various physical and chemical parameters (water content, temperature, chemical composition of fluids), and (ii) they exhibit an anisotropical texture and organization that results in observable anisotropic properties such as thermal conductivity or hydraulic conductivity.

Understanding and predicting the macroscopic behavior of these materials then clearly requires a detailed multi-scale analysis of the network in terms of both morphology (pore and particles size and shape), and topology (organization, orientation and connectivity). Special attention must be devoted to the sub-micronic scale, as many crucial processes impacting porosity (e.g. shrinkage-swelling of clays, dissolution-precipitation of carbonates leading to the filling of small pores) occur at such length scales.

We report here results obtained by neutron scattering (diffraction and small angle scattering (SAS)) on argillaceous rocks subjected to various humidity conditions. Such techniques are particularly relevant as they allow studying centimetric samples making use of neutrons high penetrating power. Furthermore, combining diffraction and SAS makes it possible to investigate the material properties of interest at different length scales. In the diffraction domain, the orientation distribution functions of the minerals constituting the rocks can be retrieved from a careful analysis of Bragg peaks intensity. In parallel, anisotropy of small angle scattering 2D patterns provides information about fabric at length scales of few tens of nanometers. Combining results from both approaches yields a relevant picture of the 3D organization of clay-rich rocks that could be further used for refining reaction-transport models in complex media.

Session A: Synchrotron source as a tool in environmental science

PA1

MICRO-SCALE INVESTIGATIONS OF THE FATE OF HEAVY METALS ASSOCIATED TO IRON-BEARING COLLOIDS IN A HIGHLY POLLUTED STREAM.

Montarges-Pelletier E.[1], Duriez C.[1], Ghanbaja J. [2], Mouton L.[2], Falkenberg G.[3], Michot L.J.[1]

[1]LEM, CNRS Université de Lorraine, 15 avenue du Charmois, BP 40, 54500 Vandoeuvre-les-Nancy, France
[2]SCMEM, Université de Lorraine, Boulevard des Aiguillettes, BP 239, 54506 Vandoeuvre Lès-Nancy
[3]Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY, Notkestr. 85, D-22603 Hamburg, Germany

emmanuelle.montarges@univ-lorraine.fr

Metallic pollution in aquatic systems represents a major environmental concern due to the persistence and toxicity of heavy metals. Studies on metaldegraded aquatic systems must analyze metal speciation in at least three compartments, the dissolved fraction, the sediments and the colloidal fraction that has been shown to play a major role in the transport and speciation of toxic substances. In solid phases, besides global metals concentrations and speciation, spatially resolved information must be obtained due to the multi-scale heterogeneity of such materials, which calls for the use of spectro-microscopic techniques. SEM and TEM provide high spatial resolution and can be advantageously combined with Energy Dispersion of X-rays Spectroscopy (EDXS), which helps in the identification of poorly crystallized phases and metallic contaminants scavengers, that can not be identified by classical XRD. However, these techniques present a few drawbacks (high vacuum conditions, beam damage, relatively high detection limits of EDXS). It is then worthwhile to combine them with X-ray based techniques such as X-ray microfluorescence and X-ray microscopy (TXM and STXM). This latter technique can be performed in wet conditions and provides spectroscopic information that can be spatially resolved at a sub-micronic scale.

In the present study, we focus on the fate and status of heavy metals in a river flowing through a dense steel making area, Fensch river. Chemical analyses reveal a significant evolution of heavy metals contents along the river linear, that is related to changes in suspended materials that are dominated by iron-bearing species. The link between those iron-bearing species and heavy metals is clearly evidenced by combining TEM and SEM observations with synchrotron based X-ray microfluorescence experiments. Further insight into iron status and oxidation state as a function of sampling station is obtained through spatially resolved STXM investigations at Fe L-edges. Data thus obtained can provide useful inputs for modeling heavy metal ecodynamics in continental aqueous systems.

PA2

SPECIATION AND FRACTIONATION OF NICKEL IN PYROMETALLURGICAL BY-PRODUCTS: CONSEQUENCES FOR ULTRAMAFIC ENVIRONMENTS

Quantin C.[1]*, Montargès-Pelletier E., [2], Jouvin D., [1], Lebreton C., [1], Gelabert A., [3], Sivry Y. [3], Pichon R.[1], Garnier J. [4]

[1] UMR 8148 IDES, UPS-CNRS, 91405 Orsay Cedex, France
[2] UMR 7569 LEM, CNRS-INPL, 54501 Vandoeuvre-lès-Nancy Cedex, France
[3] Univ. Paris Diderot – Sorbonne Paris Cité - IPGP , 75205 Paris Cedex 13 , France
[4] Instituto de Geociências, Universidade de Brasilia, CEP 70910-900 Brasília – DF, Brazil

cecile.quantin@u-psud.fr

Biogeochemical cycles of metals have been deeply modified by anthropogenic activities since the industrial revolution [1]. The major headways obtained during the last decade in the comprehension of biogeochemical cycles of metals are directly related to the strong development of X –ray Absorption Spectroscopy (XAS). Indeed, XAS is the only technique able to provide information about metal chemistry at the molecular level, i.e. solid speciation, and it allows the quantification of metal bearing species (even the diffuse ones) in dilute environmental samples with accuracy. This technology, associated to geochemical investigations about leaching stability, provides keys to understand and predict metal, here nickel, mobility and availability in environment.

Samples from the ultramafic massives of Barro Alto and Niquelândia (Goiás State, Brazil), constituted in ores, pyrometallurgical wastes (fly ash, slags), natural and waste impacted soils were characterized for their Ni speciation and extractability. The wastes contain high concentrations of Ni (1.3-23 $g\ kg^{-1}$), Fe (104-276 $g\ kg^{-1}$) and other metals like Cr. Thus, they are considered as hazardous materials, because metals can be released into the environment during weathering processes partly depending on their initial metal speciation [2], to result in fine in their potential bioaccumulation in plants.

Ni K-edge XAS data were collected in bulk and microbeam modes for Ni ore, pristine pyrometallurgical wastes before and after leaching (TCLP and DTPA procedures), to evaluate Ni extractability. TCLP or DTPA leaching leads to the extraction of 0.3 to 8.1% of Ni depending on samples. XANES spectra show that Ni is octahedrally coordinated. Linear Combination Fitting of EXAFS oscillations suggests that Ni in the ore is mainly involved in Ni-phyllosilicates and less than 20% in Ni bearing goethite. The Ni speciation in wastes is dominated by olivine and ferronickel, and leaching procedures only slightly impact Ni speciation.

To better understand Ni cycling in this environment, further investigations on isotopic signatures of Ni will be undertaken. Indeed, the relatively high temperature processes occurring during pyrometallurgy processes may be responsible of strong isotopic fractionation [3]. Hence, Ni species from slags and fly ash should be easily distinguished from natural Ni species by their different isotopic compositions. Thus, all anthropogenic materials and soils will be carefully studied for isotopic signatures, in order to better trace anthropogenic Ni in this ecosystem.

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SESSION B:

Resources and interfaces: water treatment, mineral processing, polluted soils and industrial waste remediation, bioremediation.

KB1

WATER DESALINATION USING CAPACITIVE DEIONIZATION

Biesheuvel P.M.[1,2]*

[1] Department of Environmental Technology, Wageningen University, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands.
[2] Wetsus, centre of excellence for sustainable water technology, Agora 1, 8934 CJ Leeuwarden, The Netherlands.

maarten.biesheuvel@wur.nl

Capacitive deionization (CDI) is a novel water desalination technology using oppositely placed porous activated carbon electrodes to remove ions from water [1-5], see Fig. 1a. In an important modification of the technology, ion-exchange membranes are placed in front of each electrode, which has several advantageous effects, to be discussed in the presentation [6,7]. In CDI, the electrodes first adsorb salt at a certain cell voltage, Vcell, and later release the salt again at Vcell=0 to obtain a concentrated brine. To describe CDI, tools from the field of colloid science and electrokinetics are applied such as the Nernst-Planck equation for ion transport, and electrostatic double layer (EDL) theory to describe ion storage (and not just charge) in the nanoporous carbon electrodes, for which we develop a novel "modified Donnan" approach. These elements are combined in a two-dimensional dynamical porous electrode theory to describe the time-dependent operation of CDI. The theory distinguishes between the large electroneutral transport pores (macropores) in the electrode, and the micropores inside the carbon particles in which the EDLs are formed and ions are stored, see Fig. 1b and refs [3,6]. This modeling framework is an essential tool in the design and optimization of CDI-systems.

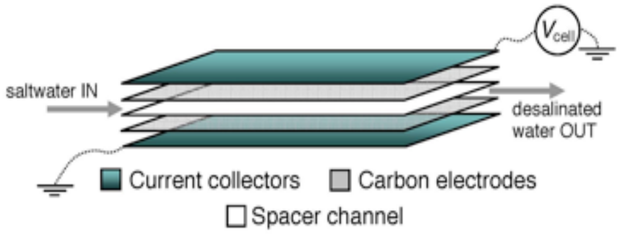

Fig. 1(a)

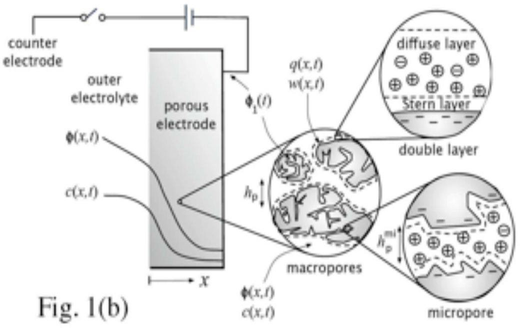

Fig. 1(b)

We show experimental and theoretical results of CDI in ion mixtures, where monovalent cations adsorbed early on, are later kicked out of the electrodes again by more slowly adsorbing divalent ions, resulting -after voltage reduction- in a water stream significantly enriched in divalent ions. This approach has potential for the selective desalination of water, the harvesting of valuable multivalent ions, and the selective removal of poisonous ions such as radionucleotides.

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RB1

ON THE REAL PERFORMANCE OF SOLID-SOLUTION SYSTEMS IN INDUSTRIAL WASTEWATER TREATMENT: COMPARISON BETWEEN ORGANIC AND INORGANIC ION EXCHANGERS

Prelot B.,*, Ayed I., Araïssi M., Marchandeau F., Zajac J.

Institut Charles Gerhardt de Montpellier, CNRS UMR 5253, Université Montpellier 2, Equipe Agrégats, Interfaces et Matériaux pour l'Energie, C. C. 1502, Place Eugène Bataillon, 34095 Montpellier cedex 5, France;

prelot@um2.fr

There have been growing concern and more stringent regulation standards throughout the world related to the discharge of heavy metals, including radionuclides, to the aquatic environment, due to their low biodegradability, high toxicity and thus inevitable adverse impact on living species. Despite major progress in the field, there is still much need either to improve the existing processes for treatment and conditioning of aqueous wastes and soils or to propose new, more efficient and low-cost technologies which will better meet the local requirements and conditions. Sorption is very attractive for removal of heavy metal pollutants from water because of (i) the ease of handling of the pollutant-loaded particles, (ii) the reduction of the volume of solid wastes to be stored in landfills, or (iii) the reversibility of the removal process thus allowing the raw materials to be preserved. When considering the implementation of such a technology, one of toughest decisions wastewater treatment operators face is choosing an appropriate sorbing material. In addition to their radiation and thermal stability, sorbents are selected on the basis of their sorption capacity towards a given pollutant. Nevertheless, the real effluents represent complex mixtures of various species competing against one another for the solid-liquid interface. The effective selectivity of sorbents is thus another important factor to be taken into account.

In the present study, the performance and mechanism of removal of heavy metals from multi-component solutions were investigated for such commercially available materials as IRN77 and IRN9652 ion-exchange resins, and 4A zeolite. Cs^+ and Sr^{2+} cations were considered in the context of their abundant occurrence in nuclear waste repositories. At first stage, the individual sorption capacities of the three ion exchangers in aqueous nitrate solutions were determined by means of ionic chromatography. Then the removal selectivity was considered thoroughly by using a mixture of Cs^+ and Sr^{2+}, in the presence of other species like Na^+, K^+, Ca^{2+} and Mn^{2+}. The composition of aqueous solutions was chosen to produce simulated effluents. The pH of the solid suspension was imposed by its composition, thereby producing acidic and basic aqueous phase in the case of resins and zeolite, respectively. Speciation of the $Me/OH^-/NO_3^-$ systems was simulated with the aid of JCHESS® software to account for the metal hydrolysis in the aqueous phase. The competitive interactions involved in the ion-exchange process were studied by using a TAM III Isothermal Titration Calorimeter (Waters, France) equipped with a titration cell. The variations of the enthalpy of displacement as a function of the amount adsorbed were rationalised to elucidate the overall uptake mechanism.

RB2

THIOL-FUNCTIONALIZED SBA-15 MESOPOROUS SILICAS AS SORBENTS OF PLATINUM (IV) IONS

Barczak M.*, Dąbrowski A., Oszust-Cieniuch M., Dobrzyńska J., Dobrowolski R.

Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20 031 Lublin, Poland

mbarczak@poczta.umcs.lublin.pl

Platinum is one of the most relevant metals present in the biosphere, particularly in the atmosphere, mainly due to the emission of exhaust gases containing precious metals originating from the abrasion and the deterioration of autocatalysts [1]. The recovery of platinum is a very important task, due to the limited world reserves, high cost and wide use in different branches of industry including electrical engineering, petrochemistry, medicine, jewellery, etc. [2].

Ordered mesoporous organosilicas (OMOs) due to their favoured adsorption characteristics (i.e. high values of specific surface areas, large pore volumes and diverse morphologies [3,4]) can be potentially employed both in industry for recovery/recycling of precious metals from wastes, and – in analytical chemistry – as sorbents used for enrichment of trace amounts of organic and inorganic analytes. An important advantage of the sol-gel synthesis of OMOs is the possibility of introduction of the organic groups with desired complexing behaviour into the structure during one-pot synthesis [5-7].

In this work mesoporous silicas functionalized with thiol ligands were synthesized, characterized and used for adsorption of Pt(IV) ions. In order to check the possibility of the application of synthesized sorbents for separation and enrichment of Pt(IV) ions from environmental samples solutions the parameters affecting on loading capacity were studied in detail. Taking into account potential analytical application of mesoporous silicas the removing of platinum species from loaded sorbents was also investigated. The obtained data testify to great usefulness of these materials towards effective adsorption and preconcentration of Pt(IV) ions.

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RB3

SILICA COATING ON WEATHERED PYRITE WASTE ROCKS TO PREVENT ACID MINE DRAINAGE

Bessho M.[1]*, Wajima T. [1], Ida T. [2], Nishiyama T.[3]

[1] Akita University, 1-1, Tegata-gakuen-cho, Akita 010-8502, Japan
[2] Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
[3] Emeritus professor of Kyoto University, Kyoto, Japan

bessho@gipc.akita-u.ac.jp

Acid mine drainage (AMD) is a serious environmental pollution issue in the mining industry. AMD is caused by the oxidation of sulfides such as pyrite, chalcopyrite, galena or sphalerite by surface or ground water. It has an extremely acidic pH value (as low as 2). Thus the effluents, released into lakes and rivers around mines, pose an immediate threat to the ecological balance. After mining ceases, AMD can also be formed when rain water passes through tailings or mine wastes in repository sites. In Japan, there are numerous closed mines. To prevent degradation of the surrounding environment, the neutralizing agent $CaCO_3$ has been added to AMD for pH adjustment and removal of metal ions as hydroxides. However, this neutralizing method must be applied almost permanently because it cannot suppress the generation of AMD completely.

A new approach to inhibit pyrite oxidation is through formation of a coating on the surface of the pyrite which would prevent both O_2 and Fe^{3+} from further oxidizing the pyrite. We have also investigate the coating on pyrite surfaces with amorphous silica. Pyrite waste rocks in repository sites are often weathred because of contact with rain water. It is considered that the pyrite surface conditions have an influence on the formation of silica coating. In this study, the formation process of silica coating on weathered pyrite is investigated.

Concentrated silica solution (pH 11, 8500 mg/L) was used for the silica coating on pyrite surfaces. The experiments were carried out on pyrite plate samples from the Yanahara mine, Japan. Some samples were oxidized with 30 % H_2O_2 solution and dried in 110 °C, prior to the experiments. The oxidized and non-oxidized samples were placed in the silica solutions (50 ml). Up to 120 hours, each sample was taken out of the solutions and dried in 110 °C. The change of the samples in the silica solutions was observed. Cross sections of the samples were also observed and characterized by s energy dispersive X-ray diffraction (EDX). No evidence of silica deposition was found for the non-oxidized pyrite sample in the silica solution even after 1 hour. To the contrary, silica was deposited on the oxidized pyrite sample in the silica solution after 5 minutes. The deposits of silica increased with an increase in incubation time, as shown in Fig. 1. Observing the veratical sections of the samples, we could confirmed that silica coating layer was thicker with an increase in incubation time (Fig. 2). The thicknesses of the coating layer in the samples placed in the silica solution for 1, 24, 72, and 120 hours were approximately 20, 70, 110, and 120 μm, respectively. EDX analysis of the vertical sections of the coated samples in the silica solution revealed that the coating layer mainly consists of silica. Thus, the formation of silica coating layer was attributed to precipitation and assembly of dissolving silica.

Fig. 1 Silica coaing on the oxidized pyrite plate. Incubation time; 120 hours

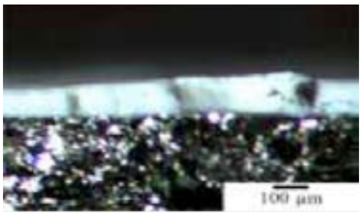

Fig. 2 Observation of the vertical section of silica coating layer

RB4

OXIDATIVE DEGRADATION OF SULFONAMIDES BY BIRNESSITE

Thiele B.[1]*, Havenith M.[2], Philipp H.[2], Klumpp E.[2]

[1] Institute of Bio- and Geosciences, IBG-2: Plant Sciences/BioSpec, Forschungszentrum Jülich, 52425 Jülich, Germany.
[2] Institute of Bio- and Geosciences, IBG-3: Agrosphere, Forschungszentrum Jülich, 52425 Jülich, Germany.

b.thiele@fz-juelich.de

Sulfonamides are a class of antibiotic pharmaceuticals which are widely used in livestock production. They reach agricultural soils and the aquatic environment mainly through the use of manure or directly through grazing livestock. To assess the potential risks of sulfonamides released into the environment a comprehensive understanding of their transport [1] and fate is required. Bio- [2] and photodegradation [3] have been recognized as possible transformation pathways of sulfonamides in soil and water. Manganese oxides like birnessite are common oxidants in soil and were used for the oxidative degradation of sulfadiazine in aqueous solution [4]. Recently the products of MnO2 mediated sulfonamide transformation have been reported [5].
Here we present the oxidative degradation of various sulfonamides (sulfadiazine, sulfamethazine, sulfamethoxazole) in the presence of birnessite. Reaction rates were followed by HPLC-UV and transformation products were identified by high resolution Fourier transformation ion cyclotron resonance mass spectrometry (FTICR-MS) and liquid chromatography-mass spectrometry (LC-MS). The obtained products included oxidized sulfonamides, SO_2 extrusion products and dimeric products.

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RB5

VISIBLE LIGHT-MEDIATED DEGRADATION OF CONTAMINANTS BY APPLICATION OF AG@AGCL PHOTOCATALYSTS EMBEDDED ON REDUCED GRAPHENE OXIDE

Miller C.[1]*, Yu H.[1], Waite T.D.[1]

[1] School of Civil and Environmental Engineering, The University of New South Wales, Sydney, New South Wales, 2052, Australia

c.miller@unsw.edu.au

The use of visible light to effect chemical transformation shows significant promise as a technology to degrade organic pollutants, with potential improvements in simplicity and cost-effectiveness over existing photochemical technologies employing UV light. The preparation of a hybrid photocatalyst consisting of Ag^0/AgCl particles embedded upon sheets of reduced graphene oxide has recently been reported by Zhang et al. [1] with the effectiveness of this system at decolourizing solutions of rhodamine b demonstrated, however, few insights into the mechanism of degradation or factors important to optimizing the process have been elucidated. We have synthesized similar particles, examined in further detail the degradation of rhodamine b and also utilized radiolabelled formic acid as a target compound. Studies employing formic acid greatly simplify the system as formic acid degrades following a simple and well known pathway and also does not absorb the visible light employed for photocatalysis, allowing for mechanistic insights into the degradation mechanism to be made. Measurements of formic acid degradation coupled with measurements of reactive oxygen species concentration allowed significant insights into the mechanism of these particles to be made and the potential intermediacy of reactive oxygen species to be examined.

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RB6

EFFICIENT INHIBITION OF BROMATE FORMATION BY SURFACE REDUCTION ON β-FEOOH/AL$_2$O$_3$ WITH OZONE

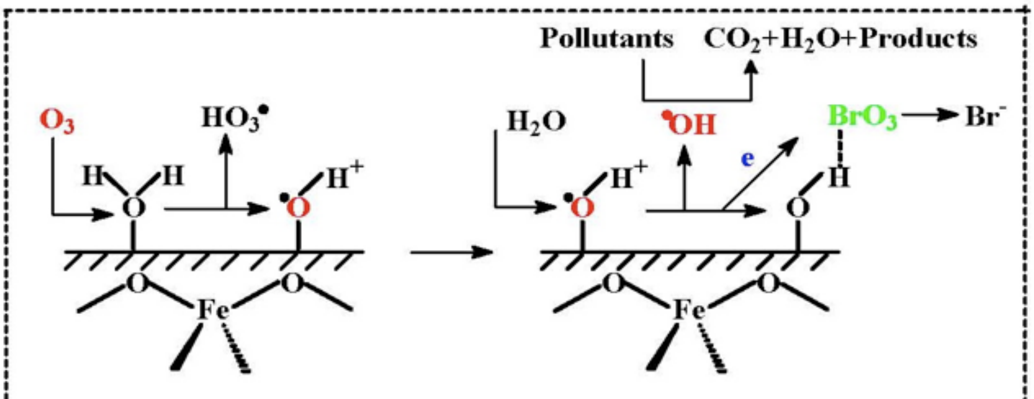
Nie Yulun*, Hu Chun*, Yang Min, Qu Jiuhui

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ylnie@rcees.ac.cn; huchun@rcees.ac.cn

For drinking-water ozonation treatment, production of bromate from bromide remains an important challenge. The inhibition mechanism of BrO_3^- formation was investigated in detail during the catalytic ozonation of organic contaminants over mesoporous alumina supported β-FeOOH (β-FeOOH/MA). The catalyst exhibited both complete inhibition of bromate formation and the most efficient catalytic ozonation of pollutants. Adsorbed bromate was reduced to bromide on the surface of β-FeOOH/MA with ozone during the degradation of pollutants. On the basis of *in situ* diffuse reflection UV-vis spectra and cyclic voltammetry analyses under a variety of experimental conditions, a surface-reduction mechanism of inhibition bromate formation was verified in β-FeOOH/MA suspension, wherein the catalyst underwent oxidation and reduction with adsorption and decomposition of ozone by substituting surface-adsorbed water or surface hydroxyl groups, which were oxidized to surface-adsorbed $^{\bullet}OH$. The bromate formed from the oxidation of bromide was adsorbed and reduced with desorption of surface-adsorbed $^{\bullet}OH$, enhancing free $^{\bullet}OH$ generation and leading to greater removal of pollutants.

This finding indicates that the proposed mechanism and the designed catalyst could be applied toward the abatement of bromate formation and process adjusting for ozonation of bromide-containing drinking water.



Surface oxidation and reduction reaction mechanism

RB7

THE EFFECT OF TRANSITION METAL SUBSTITUTION ON THE CATALYTIC ACTIVITY OF MAGNETITE IN HETEROGENEOUS FENTON REACTION: IN INTERFACE VIEW

Liang Xiaoliang,[1,2] , Zhong Yuanhong[1,2], He Hongping[1]*, Yuan Peng[1], Zhu Jianxi[1]

[1] Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences, Guangzhou 510640, China.
[2] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China.

hehp@gig.ac.cn

The growing interest in transition metal substituted magnetites used as heterogeneous Fenton catalysts in the degradation of organic pollutants has been evoked, due to high efficiency around neutral pH, easy recycle in practical application and prevalence as natural minerals. In the present study, the effect of substitution on the heterogeneous Fenton catalytic activity of magnetite was investigated in interface view. The substitution improved the catalytic activity of magnetite through the enhancement of the pollutant adsorption and hydroxyl radical $^{\bullet}$OH production. For instance, Ti and Cr increased the BET surface area and superficial hydroxyl amount of magnetite, resulting in larger methylene blue (MB) adsorption and accordingly faster degradation. The increase of superficial hydroxyl also enhanced the complexation between H_2O_2 and superficial hydroxyl, which triggered the $^{\bullet}$OH production. As the octahedral sites are exclusively exposed at magnetite surface, V^{3+} and Cr^{3+} at the octahedral sites could decompose H_2O_2 to produce $^{\bullet}$OH and accelerate the electron transfer during the reaction. Under neutral pH condition, the MB degradation followed the L–H mechanism (i.e. reaction of adsorbed MB with $^{\bullet}$OH engendered on magnetite surface) and was described by the zero–order kinetics. But the acid orange II (AOII) degradation followed the E–R mechanism (i.e. reaction of dissolved AOII with $^{\bullet}$OH produced on magnetite surface) and was fitted with the two−stage first−order kinetics. These results will be benefit for the application of transition metal substituted magnetite in environmental engineering.

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RB8

DEGRADATION OF ORGANIC POLLUTANTS IN ANCIENT COKING PLANT SOILS: REACTIVE MINERALS EFFECTS DURING AIR OXIDATION

Faure P.*, Biache C., Kouadio O. , Lorgeoux C.

G2R UMR CNRS 7566, Université de Lorraine, BP 239 54506 Vandoeuvre les Nancy, France

pierre.faure@g2r.uhp-nancy.fr

Among different processes occurring in contaminated soils in natural attenuation context, air oxidation must be considered. Previous experimental works on real soils as well as on model contaminant, have revealed that organic contaminants, especially PAH (Polycyclic Aromatic Hydrocarbons), can be affected by air oxidation. Experiments on real soils demonstrate that air oxidation is able to decrease the concentration of PAH [1]. On the other hand, model compounds experiments suggest that this decrease in PAH content, is associated to the condensation of aromatic cycles [2]. Moreover, this condensation seems to be favour by the occurrence of reactive mineral phases.

This work presents experiments carried out at an intermediate scale between simplified system (model compounds) and real complex soils. In a first step, extractable organic matters (EOM) isolated from two real coking plant soils were artificially oxidized (60°C and 100°C) during 5 months on the presence of three different mineral phases: Fontainebleau sand, goethite and smectite).

Then, the same experimental conditions (time, temperature and mineral phases added) were carried out with the integral soils including EOM, insoluble organic matter (IOM) and native mineral phases. The evolution of the EOM as well as IOM were studied at molecular and spectroscopic scales and confirms (i) the ability of air oxidation to remove PAH contaminant by condensation processes and (ii) the catalytic properties of reactive minerals to accelerate such transformations.

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KB2

EXPLORATORY RESEARCH: LOW-FREQUENCY ACOUSTIC ENERGY-ENHANCED BACTERIAL TRANSPORT IN POROUS MEDIA

Johnson O.,[1]* Charles M. N.[2]

[1]Claflin University, 400 Magnolia Street, Orangeburg, SC, 29115, USA.
[2]Claflin University, 400 Magnolia Street, Orangeburg, SC, 29115, USA.

oljohnson@claflin.edu

Major technological challenge facing biostimulation for bioremediation is poor bacterial transport and dispersion in saturated porous media, due to bacterial adsorption dictated by media-biological properties. Adsorption and consequent filtration extent govern media permeability and ultimate bacterial seeding of contaminated zones. Existing permeability augmentation technologies required that media pH/ORP, fluid injection rates, bacterial strain selection with desired transport or genetic properties, or alternate nutrient-bacterial inoculum injection be manipulated singly or in combination in order to enhance bacterial transport in porous media. Changing pH/ORP of the media, which governs the extent of van der waal and electrostatic forces controlling bacterial-media attractive/repulsive forces may promote bacterial adhesion to media surfaces and accelerate biosorption of adherent colonies. Thus, an alternative technique requiring little or no manipulations of media physicochemical and biological properties is needed to accelerate bioremediation processes. Low-frequency energy stimulation has been demonstrated to enhance crude oil flow during earthquakes [1], dense nonaqueous liquids (DNAPLs) such as trichloroethylene [2,3], solute [4] and inferred clay [5] transport in saturated porous media. To date, the potential of low-frequency acoustic energy stimulation for augmenting bacterial transport for insitu bioremediation has not been studied. Low-frequency acoustic energy propagates through porous media with little attenuation and it's environmentally-friendly.

This exploratory study focused on establishing the feasibility of using low-frequency (1-1000 Hz) acoustic energy stimulation for enhanced-P. *fluorescens*-Pf5 transport in saturated porous media. Glass bead (1-2 mm) packed column fitted with acoustic hardware and flow-through bacterial inoculum were stimulated with different frequencies under constant fluid flow conditions. Experimental pH/ORP, acoustic pressure, electrical conductivity, temperature, permeability, chloride and bacterial concentrations were monitored. Relative permeabilities and breakthrough curves of *P. fluorescens*-Pf5 transport under no acoustic and acoustic stimulation conditions were normalized to those of conservative chloride as functions of frequency, pore volume and time. Acoustic energy stimulation may be used as a potential stand-alone technology or as an adjunct to the existing physicochemical augmenting biostimulation technologies requiring nutrient-rich water such as biologically enhanced-secondary oil recovery and bioremediation.

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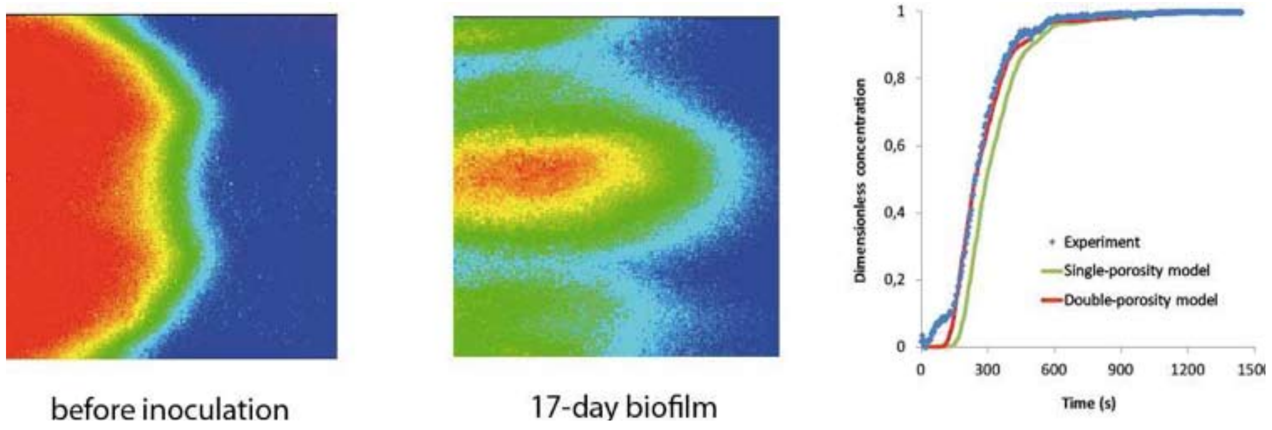
NUMERICAL AND EXPERIMENTAL INVESTIGATION OF COUPLED PROCESSES AFFECTING TRANSPORT OF AN ORGANIC POLLUTANT IN BIOFILM-COATED POROUS MEDIA

Kone T.[1]*, Golfier F.[1], Orgogozo L.[2], Oltéan C.[1], Buès M.[1]

[1] Laboratoire Environnement, Géomécanique et Ouvrages, Université de Lorraine, Rue du Doyen Roubault - BP 40 F - 54501 Vandoeuvre-lès-Nancy, France
[2] Géosciences Environnement Toulouse, 14 avenue Edouard Belin, 31400 Toulouse, France

tiangoua.kone@ensg.inpl-nancy.fr

In subsurface systems, biofilm may degrade organic or organo-metallic pollutants contributing to natural attenuation and soil bioremediation techniques. Biofilm accumulation, however, decreases free pore space thereby decreasing media porosity and permeability while increasing hydrodynamic dispersion (e.g., [1]). This mechanism commonly referred to as bioclogging may thus influence the success of bioremediation methods in polluted aquifers. The overall goal of this work is to to gain a better understanding of biofilm growth processes in porous media and how these processes affect macroscopic flow and transport properties. To achieve this goal an experimental device was performed. A flowcell containing quartz sand colonized with biofilm (*Shewanella oneidensis* MR-1 species) was used for monitoring both biofilm growth and solute transport. The biofilm volume fraction was estimated through tracer experiments with a macromolecular tracer (i.e., Blue Dextran) as in size-exclusion chromatography or gel filtration chromatography. After 29 days of bacterial culture, the volume fraction of biofilm was 50% of void space volume. The influence of biofilm growth on porous media transport properties was evaluated. Breakthrough curves were compared with numerical simulations. Single- and doubleporosity models were investigated [2]. A transition from a fickian transport behavior to a non-fickian one due to the microbial activity has been observed.



before inoculation

17-day biofilm

Figure 1. Solute transport in the porous medium before inoculation and after 17 days - Comparaison between experimental and numerical breakthrough curves at t=17 days

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RB10

MICROBIAL AND CHEMICAL CHARACTERISTICS IN THE REMOVAL OF LANDFILL ODORS BY AN INTEGRATED-BIOREACTOR

Li L.*, Liu J.X.

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18
Shuangqing Road, Haidian District, Beijing 100085, P.R. China

leel@rcees.ac.cn

A large number of volatile organic compounds and odors will be generated when municipal solid wastes decompose in landfill sites. Those areas that not use temporarily were covered by high density polyethylene (HDPE) film in order to prevent the emission of VOCs and odors. However, they will accumulate under the films and still pose a threat to human health and the environment. Compare with conventional physical-chemical methods, biological technologies, such as biofilters, bioscrubbers and biotrickling filters, have been widely applied owing to their efficiency, cost effectiveness and environmental acceptability. Eleven full-scale integrated-bioreactors were set up to remove H_2S and NH_3 accumulated under the HDPE films in a landfill site with an area of 16000 m^2, in Beijing. The integrated bioreactor consisted of a suspended zone and an immobilized zone.

Results showed that the inlet concentrations of H_2S and NH_3 were 9.54-23.09 mg/m^3 and 0.13-1.79 mg/m^3, respectively. The outlet concentrations reduced to 0-1 mg/m^3 for H_2S and 0.1 mg/m^3 for NH_3. Both H_2S and NH_3 could be eliminated effectively by using the integrated bioreactor. In steady state, the total removal efficiencies were over 90%. Their removal efficiencies were different from one zone to the other. The results from bio-products analysis indicated that most of H_2S was bio oxidized into element sulfur and sulfate in the immobilized zone while most H_2S was dissolved into the liquid phase in the suspended zone. Much more NH_3 was transformed into nitrate and nitrite by nitration in the suspended zone, only a few of NH_3 transferred to aqueous phase mainly by absorption or chemical neutralization in the immobilized zone. SEM provided detailed images of the distribution of total sulfur on packing material. Sulfur filaments can grow either on the surface or within the media, but most sulfur accumulated on the packing media's surface. The pure-culture method and PCR DGGE based method were applied to describe concentration, species diversity and distributions characteristics of microorganisms in the integrated bioreactor. Four species of microorganisms which related to the degradation of H_2S and NH_3 were isolated. Their characteristics and distributions in the bioreactor depended on the inlet concentration of substrates and microenvironment in the individual zone.

RB11

MODELLING NICKEL MOBILITY IN MINING SPOILS FROM ULTRAMAFIC LATERITES

Raous S.[1], Hanna K.[2], Thomas F.[3], Becquer T.[4], Sterckeman T.[1], Echevarria G.[1]*

[1]LSE, UMR 1120 Université de Lorraine – INRA, Vandoeuvre-lès-Nancy, France.
[2]LCPME, UMR 7564 Université de Lorraine – CNRS, Villers-lès-Nancy, France.
(Present address: .Sciences Chimiques de Rennes UMR ENSCR – CNRS 6226, Rennes, France)
[3]LEM, UMR 7569 Université de Lorraine – CNRS, Vandoeuvre-lès-Nancy, France.
[4]Eco&Sols, UMR 210 Supagro – INRA – IRD, Antananarivo, Madagascar.
Guillaume.Echevarria@univ-lorraine.fr

Ultramafic mining spoils contain potentially toxic trace metals (TM) (*e.g.* Ni, Cr, Cu, Mn) which could diffuse in the environment, and cause ecosystem dysfunctioning or human intoxication [1]. To decrease the risk created by these wastes, the first step is to understand the reactions governing the TM mobility. A preliminary study [2] allowed the precise identification of the reactive metal bearing phases present in the spoils. Among these, a Ferich smectite and goethite were carefully studied for their reactive properties and characteristics and especially towards TM. Sorption isotherms of the major elements present in the spoils onto the two minerals were carried out to determine their sorption properties under different environmental situations. The first step of this study was to analyse the composition of suspensions of garnieritic (smectite-rich) and limonitic (goethite-rich) spoil in contact with extractants of different strength (water, $NaNO_3$, citrate and EDTA) in column experiments [1]. The use of complexing agents (citrate and EDTA) aims to mimics the effect of roots exudates on trace metal elements mobilisation. In a second step, these compositions and sorption isotherm data were used in the modelling step (PHREEQC model) in order to understand if inner and outer sphere complexation reactions were indeed sufficient mechanisms to explain Ni and Cr mobility in ultramafic mining spoils. Nickel concentrations in water eluted stabilized around $2.0\ 10^{3}$ mM in both garnieritic and limonitic columns. In The Ni concentrations in garnieritic columns were $2.5\ 10^{-2}$ and $3.0\ 10^{-2}$ mM in presence of 10 mM Citrate and EDTA ligands respectively. In limonitic columns they were of respectively $4\ 10^{-3}$ and $3\ 10^{-3}$ mM for the same ligands used. At the goethite and smectite surface, the main reactions involved in Ni release were indeed inner (goethite) and outer sphere (smectite) complexation as confirmed by the success in modelling Ni speciation in solution using PHREEQC and isotherm data. Even though for garnierite, outer sphere complexation seems to be sufficient to explain mobility, more complex phenomena – such as the formation of silicated precipitates – have to be considered to explain Ni mobility in limonitic spoil. Furthermore, in oxidic spoils, Cr (*i.e*. mainly under CrVI) seems to be much more problematic than Ni as its mobility, especially in presence of organic acids, is much greater than for Ni [1].

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RB12

SUSTAINABLE DEGRADATION OF NITROPHENOLS IN THE RHIZOSPHERE OF *SPIRODELA POLYRRHIZA* USING RHIZOAUGMENTATION

Kristanti R.A.*, Toyama T., Tanaka Y. ,Mori K.

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-3-11 Takeda, Yamanashi, 400-8511 Japan

g09dea06@yamanashi.ac.jp

Nitrophenols are industrially important chemicals mainly used for production of pharmaceuticals, dyes, plasticizers and explosives [1]. As a consequence, they are abundantly presented in aquatic environments including river water, wastewater, and industrial effluents [2]. The U.S. Environmental Protection Agency [3] has listed 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), and 2,4-dinitrophenol (2,4-DNP) as priority pollutants. Thus, the study of NPs biodegradation is necessary for establishing technologies to treat water polluted by NPs and to remove NPs from contaminated environments. In this study, the stability of the 2-NP, 4-NP and 2,4-DNP removal ability of an association between giant duckweed (Spirodela polyrrhiza) and bacteria were investigated in 5-cycles repeated batch experiments (equivalent to 10 days where each cycle was done for 2 days). Three different kinds of water (contaminated water treatment, river water and Hoagland nutrient solution) were selected to evaluate the effect of introduced bacteria (*Pseudomonas sp*. ONR-1 and *Rhodococcus sp.* DNR-2) in the system. The rate of 2-NP, 4-NP and DNP removal by the *S. polyrrhiza*-introduced bacteria association were higher than that by *S. polyrrhiza*-indigenous bacteria association through 5 cycles. The NPs removal ability of the the *S. polyrrhiza*-bacteria association rapidly increased after exposure to NPs, with concomitant a notable increase in the population of total culturable NPs-degrading bacteria. Beside 2-NP, after NPs acclimation, the enhanced NPs removal ability of *S. polyrrhiza*-introduced bacteria association was maintained in the long term, with a high population. Since the ability of nitrophenols-degrading bacteria to survive in a wide range of environmental condition is of interest for bioremediation of nitrophenols-contaminated water. Hence, the rhizougmentation using introduced NPs-degrading bacteria could be an effective and stable treatment technology for organic pollutants.

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RB13

STABILIZATION OF ARSENIC, CHROMIUM AND COPPER POLLUTED SOIL BY IRON OXIDE AMENDMENT

Nielsen Sanne Skov*, Kjeldsen Peter, Jakobsen Rasmus J.

DTU Environment, Technical University of Denmark.

ssko@env.dtu.dk

Iron oxide forming compounds have been used at former wood impregnation sites polluted with copper, chromium and arsenic (CCA) as soil amendment for chemical stabilization of contaminants in soil [1,2]. In this study iron oxide containing water treatment residue (WTR) was added to a CCA contaminated soil to successfully reduce the leaching of arsenic, chromium and copper both at laboratory and field scale. WTR is an iron rich waste product from the treatment of groundwater to drinking water. It consists mainly of ferrihydrite, a low ordered iron oxide, with a high potential for sorption of ions [3]. The method has been tested at the former Collstrop Wood Impregnation Plant in Hillerød, Denmark. The site is heavily polluted with As, Cr and Cu, mainly present in the top soil. Pollution occurred as spill of impregnation liquids together with disposal of bark removed from impregnated logs. For more than 30 years mainly the arsenic has been leaching from the soil to the secondary groundwater which discharges into a ditch system connected to the protected Esrum Lake. Batch leaching tests on soil from the Collstrup site has previously demonstrated the potential of the stabilization method in the laboratory. When mixing heavily polluted soil (1000 mgAs/kg and 600 mgCr/kg) with 5% dw of WTR, the leaching was reduced with 99% for arsenic and 98% for Cr [4]. Subsequent a field experiment was made to evaluate the practical application of the method. Two sites of 100 m^2 were established, one with 3 % dw WTR amendment and one where the soil had been mixed, but no WTR was added. The soil was mixed down to a depth of 1 meter. Pore water samplers were installed to monitor the development of As, Cr, Cu and Fe concentrations. Data collection is still in progress at the site, and will be concluded spring 2012. So far it seems, that even after a possible iron reducing period, the treated soil still efficiently retains especially As and Cu. However efficient mixing and a sufficient amount of WTR are crucial to obtaining adequate retention. Consequently we recommend water treatment residues as an economically favorable amendment for arsenic and chromium polluted soil that effectively minimizes leaching.

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REMOVAL BEHAVIOR OF PHOSPHATE FROM AQUEOUS SOLUTION BY CALCINED PAPER SLUDGE

Wajima T., [1]* Rakovan J. F.[2]

[1]Akita University, 1-1, Tegata-gakuen-cho, Akita 010-8502, Japan
[2]Miami University, 250 S. Patterson Ave. Shideler Hall, Oxford OH 45056-2437, USA

wajima@gipc.akita-u.ac.jp

Paper sludge is generated as industrial waste during the manufacture of recycled paper products, and discharged amounts are increasing annually. Although a small portion of the sludge has been used as a fertilizer, burial in landfills, damping at sea, most is incinerated and dumped in landfills. The large daily output of paper sludge and the limited landfill capacity causes social and environmental problems.

In this study, paper sludge is converted into an effective sequestration agent of phosphate (PO_4^{3-}) through calcination, and removal behavior of the obtained product for phosphate ion from aqueous solution was examined, because development of a feasible method for removing and recovering phosphate from wastewater is required to improve eutrophication of lakes, bays, and inland seas.

Paper sludge contains mainly cellulose fibers and inorganic fillers together with coating materials such as calcite, kaolinite and talc. The sludge was fired at temperatures between 200 – 1000°C for 6 h. Crystalline phases originally present altered at increasing temperatures (up to 800°C) in the order kaolinite < calcite < talc. An amorphous phase was formed at 800°C, and gehlenite was formed at 1000°C. Paper sludge fired at 800° C, which has amorphous phases, showed the highest uptake of phosphate ion (Fig. 1), and phosphate uptake was almost constant in pH range between 5 and 12. It also shows high selective removal for PO_4^{3-} in solution with coexisting Cl^-, NO_3^- and SO_4^{2-}. The equilibrium removal ability of the product used for phosphate ion was measured, extrapolated using Langmuir and Freundlich isotherm models, and experimental data are found to fit Langmuir than Freundlich. Removal kinetics was tested for pseudo-first order and pseudo-second order reaction, and the rate constants for these kinetic models were calculated. Removal experiments demonstrate that the removal process corresponds to pseudo-second order kinetics model than pseudo-first order model. With increasing temperature of aqueous solution, the kinetics of removal becomes faster and the removal amount of phosphate increases. The thermodynamic values, ΔG^0, ΔH^0 and ΔS^0, indicated that removal reaction was an endothermic and spontaneous process. The main process responsible for sequestration of PO_4^{3-} is the formation of brushite [$CaHPO_4 \bullet 2H_2O$] by reaction between labile Ca and PO_4^{3-} in the solution. From an economic point of view, calcined paper sludge is an inexpensive raw material for phosphate ion removal from aqueous solutions.

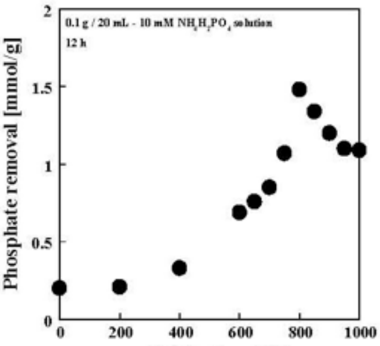

Figure 1. Phosphate removal on the product prepared at various calcination temperatures.

RB15

EFFECT OF CALCINATION ON THE STABILITY AND LEACHABILITY OF ARSENIC IN THE ARSENIC BEARING FERRIC AND MANGANESE BINARY OXIDE

Wang Hongjie[1, 2]*, Xu Meng[1], Lei Di[1], Zhai Yujia[1], Li Yaxuan[1], Qu Dan[1, 2]

[1] College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China
[2] Beijing Key Lab For Source Control Technology Of Water Pollution, Beijing 100083, P.R. China

whj_99@126.com

After safely and quickly treatment of arsenic polluted water, a great amount of arsenic-bearing solid residuals (ABSR) were left to be disposed correctly. In present study, the effect of calcination on the stability and leachability of arsenic in the arsenic-bearing Ferric and Manganese Binary Oxide (AB-FMBO) and the possibility of manufacturing calcined bricks with AB-FMBO were explored. To the AB-FMBO with arsenic concentration of 103 g/kg, the stability of arsenic in the calcined AB-FMBO was a little bit decreased with the increase of the calcining temperature. The ratio of arsenic stabilized in the calcined AB-FMBO was 98.84%, 98.65%, 98.17% and 97.88% at calcining temperature of 700, 800, 900 and 1000°C, respectively. The leachability of arsenic in the calcined AB-FMBO was inverse proportion with the calcining temperature. The leachate of the AB-FMBO calcined at 700, 800, 900 and 1000°C was conducted by toxicity characteristic leaching procedure (TCLP) and the arsenic concentrations of the leachate were 0.696, 0.362, 0.305 and 0.118 mg/L, respectively. The specific surface area, pore volume and BJH pore diameter of the calcined AB-FMBO were all decreased with the increase of the calcining temperature. According to the results of EDX and acid digestion procedure, the ratio of surface arsenic concentration in the calcined AB-FMBO was 10.65%, 10.03%, 9.88% and 6.36%, while the ratio of the total arsenic concentration of the calcined AB-FMBO was 11.68%, 11.79%, 11.74% and 12.36%, respectively. XRD pattern showed the transformation of the amorphous AB-FMBO into hybrid crystal of AB-FMBO. The mole ratio of Mn to Fe was 0.983 to 0.017. FTIR results indicated the formation of the band of As-O-Fe and the intensity of the band became stronger according to the increase of calcining temperature. In view of the high stability and low leachability of the arsenic in the AB-FMBO, the procedure of manufacturing calcined bricks was a feasible treatment method for the disposal of AB-FMBO.

Keywords: Arsenic-bearing solid residuals, Ferric and manganese binary oxide, Calcined bricks, Stability, Leachability

RB16

COPPER-CYANIDE COMPLEX REMOVAL BY A NOVEL DUAL FUNCTION POLYALUMINUM CHLORIDE

Hu C.Z., You L.Y., Lan H. C., Zhao X., Liu H.J.*, Qu J.H.

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for
Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

hjliu@rcees.ac.cn

Wastewater from electroplating and gold mine industries often contain copper(I)-cyanide complexes. Based on the CN/Cu molar ratios copper(I)-cyanide complexes form $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$ in aqueous solution, the stability constants of these compounds are 24.0, 28.6 and 30.3, respectively. They are very toxic, and the complexed Cu is difficult to be removed by conventional methods. Effective treatment for the removal of copper(I)-cyanide complexes is needed before discharging these compounds into environment. The addition of oxidizing chemicals is the most popular procedure to destroy and remove cyanide [1], and then Cu(II) is available to be removed by chemical precipitation and coagulation etc [2]. An electrochemically prepared water treatment reagent containing a high concentration of Al_{13} polymer and active chlorine (PACC) showed promising potential to remove copper-cyanide complexes due to the combined function of oxidation and coagulation. The removal mechanism of copper-cyanide complexes by PACC is: cyanide oxidation by active chlorine and subsequent Cu(II) removal by Al_{13} polymer coagulation.
Complete treatment of cyanide by active chlorine in PACC undergoes two stages (Formula 1 and 2):

$$2[Cu(CN)_3]^{2-} + 7ClO^- + H_2O = 2Cu^{2+} + 6CNO^- + 7Cl^- + 2OH^- \qquad (1)$$
$$2CNO^- + 3ClO^- + H_2O = N_2 + 3Cl^- + 2HCO_3^- \qquad (2)$$

The reactions of cyanide and cyanate with active chlorine were monitored using stopped-flow spectrometer. The results showed that the rates of the two reactions decreased with increasing pH. The first stage oxidation of cyanide to cyanate is best carried out batch-wise at a pH of around 11, and complete reaction need about 15 minutes. The Al13 polymer was the most active Al species responsible for Cu(II) removal in PACC. Considering the process of Cu(II) coagulation and CNO^- oxidation together, the optimum pH condition to remove copper-cyanide complexes by PACC for the second stage is at 8. The second stage involves the conversion of cyanide to nitrogen and carbonates, and complete reaction need about 40 minutes at pH 8. Under the pH condition of the two stages examined in this study, the stoichiometric ratio of active chlorine to cyanide for the decomposition to nitrogen and carbonates is found to be approx 7 mg Cl_2/ mg CN^-. For the model water of 10 mg/L $[Cu(CN)_3]^{2-}$, after the two stages treatment at PACC dosage of 24 mg Al/L (weight ratio of Cl_2/Al within the used PACC was 3) the residual CN^-, CNO^-, and Cu(II) can meet the emission standard of pollutants for electroplating.

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RB17

SEPARATION OF TENNANTITE FROM CHALCOPYRITE: ATOMIC FORCE MICROSCOPY AND UV-VIS SPECTROSCOPY STUDY

Petrus H.T.B.M.[1,2], Hirajima Tsuyoshi[1], Sasaki Keiko[1], Okamoto Hideyuki[3]

[1]Faculty of Engineering, Kyushu University, Japan
[2] Department of Chemical Engineering, Gadjah Mada University, Indonesia
[3]Sumitomo Metal Mining Co., Ltd., Japan

hirajima@mine.kyushu-u.ac.jp

Arsenic possesses danger to human life and environment. Therefore, separation of tennantite, one of the arsenic bearing copper minerals, from chalcopyrite has grasped researcher`s interest, recently. In this study, effect of pH was applied into both single mineral and arseno copper ore flotation study. Possible separation can be conducted in alkaline condition represented by the floatability results. In particular, Atomic Force Microscopy (AFM) was used to observe the morphology and surface characteristic of tenanntite and chalcopyrite after treatment. It was found that new surface "island" was formed on both minerals. The occurrence of the islands as product of reaction amplified along with time treatment. From the measured adhesion force, it was indicated that the formation of islands in acid condition brought the adhesion force value lower than in alkaline condition showing the more hydrophobic characteristic to the minerals surface.

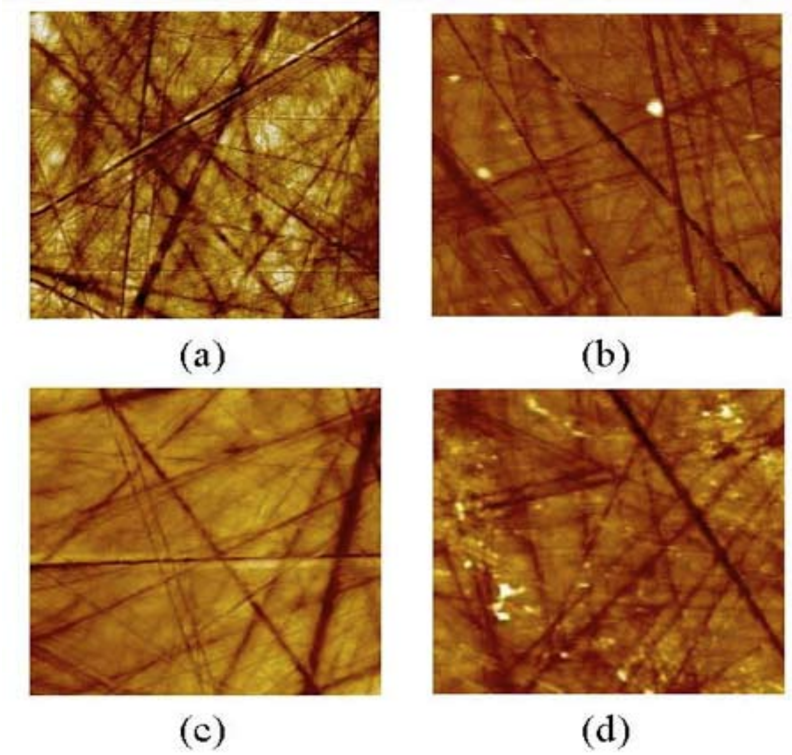
(a) (b) (c) (d)

Figure 1. AFM images of chalcopyrite treated at pH 9 (a) initial condition (b) after 60 minutes; tennantite (c) initial condition (d) after 60 minutes. The dimension of the image is 5×5µm.

The more hydrophilic surface of both minerals indicated by higher value of adhesion force at alkaline condition is due to the occurrence of hydroxide moieties on the mineral surface. In addition, it shows the reactivity of the minerals in which tennantite possesses higher reactivity than chalcopyrite. Furthermore, the microscopic observation using AFM was consistent with the findings of contact angle and floatability study representing the macroscopic observation. Adsorption of DTP on both minerals has also been studied using UV-visible spectroscopy showing the inhibition of hydroxide moieties on DTP attachment in which tennantite inhibits higher.

RB18

REACTIVITY AND FATE OF IRON AND IRON/NICKEL NANOPARTICLES IN URANIUM CONTAMINATED WATER

Riba O.[1]*, Grivé M.[1], Scott M. T. B.[2]

[1]Amphos 21 Consulting, S.L., P. Garcia Fària 49-51, 1-1. Barcelona, E-08019 Spain.
[2]University of Bristol, Interface Analysis Centre, 121 St Michael's Hill, Bristol BS2 8BS, U.K.

olga.riba@amphos21.com

Iron based bimetallic nanoparticles have been successfully used in field experiments to remediate waters contaminated with chlorinated hydrocarbons. Extensive comparative studies under anoxic conditions investigating Fe and Ni/Fe bimetallic nanoparticles have demonstrated that the latter increases the effectiveness of dechlorination of high concentration chlorinated aliphatic hydrocarbon solutions (Barnes et al. [1]). Recently, studies dealing with Fe and Ni/Fe nanoparticles reactivity towards contaminated effluents arising from industrial processes (Dickinson and Scott [2, 3], Crane et al. [4]) showed the high efficacy of the studied nanoparticles to immobilize uranium at relatively short equilibration times. The current study focused on the fate of Fe and Ni/Fe nanoparticles in uranium containing solutions under oxic conditions at longer reaction times (up to 41 days). In order to develop a fundamental understanding of uranium removal behaviour of iron-based nanoparticles under oxic conditions, thermodynamic simulations of the studied systems were performed and compared with the experimental data obtained from solution analysis (pH, Eh and total concentration of Fe, Ni and U) and characterization of residual solid phases by XPS, FIB, TEM, and XRD. The results indicated that magnetite was the predominant iron-phase, driving the redox potential of the system. Under these conditions, reductive precipitation of aqueous uranyl to form a partially reduced oxide precipitate (UO_{2+x}) is demonstrated by U 4f XPS measurements on the surface of both studied nanoparticles at reaction times smaller than 3 days. At longer reaction times, the characterization of the system with iron nanoparticles reveals that most of uranium was released back to solution. However, U re-release in the system with iron/nickel nanoparticles was limited by the formation of a secondary uranium phase determined to be isostructural to becquerelite containing α-U_30_8 anion-topology, as identified by XPS and XRD. This determination is in agreement with thermodynamic calculations, which have also been used to confirm experimental measurements for different water compositions [2-5] giving an inside of the short and long term behaviour of iron based metallic nanoparticles used for remediation of uranium contaminated waters.

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RB19

USING CHLORINE DIOXIDE AS PRE-OXIDATION COMBINE WITH LOW pH COAGULATION TO ENHANCE THE REMOVAL OF NATURAL ORGANIC MATTERS.

Wu Chih-Chao*, Chang I-Wen, and Wu Jerry J.

Department of Environmental Sci. & Eng, Feng-Chia University, 100 Wenhwa Rd. Seeton, Taichung, Taiwan
Phone: +886-4-24517250 ext5213 Fax: +886-4-24512405

Correponding author

The objective of this research was to characterize the effects of chlorine dioxide on organic matter removal, coagulation/sedimentation efficiency, and disinfection by-products (DBPs) formation in raw water from the Cheng-Kong reservoir. Cheng-Kong reservoir is the major raw water source for water supply in Ponhu Island. Because the precipitation is the only one influent for this reservoir during typhoon visiting and the strong evaporation is always happened on the others day, the organic matter removal and DBPs reduction are highly concerned for water treatment facility. Low pH coagulation or Enhanced Coagulation is an effective way to increase the removal of organic matter during the coagulation/sediment process. Chlorine dioxide can play a good performance on the oxidation and disinfection to remove organic matter and avoid the formation of THMs. Under an acid environment, the formation of ClO_2^- and ClO_3^- are avoided after the addition of Chlorine dioxide. This study was proposed to test a process combine the pre-oxidation by chlorine dioxide with the coagulation in low pH condition to increase the organic matter removal and avoid the ClO_2^- and ClO_3 formation. The tests were processed under the coagulation with the condition of pH=5.5, 7.0 and the enhance coagulation combined the pre-oxidation by chlorine dioxide with different dosage and reaction time to increase the NOM removal and decrease the DBPs formations.

The removal of DOC and A254 are insignificantly enhanced in raw waters with the addition of chlorine dioxide as the pre-oxidation. The results showed that changing coagulation conditions provides greater removal efficiency of organic matters than adding chlorine dioxide. The organic matter removal efficiencies of various processes set are listed in descending order: traditional coagulation at pH 5.5 > enhanced coagulation at pH 6.3 > traditional coagulation at pH 7.0. The chlorine dioxide pre-oxidation is able to breakdown large molecules (0.45µm ~10 K) into small molecules (< 1K). From the fluorescence intensity measurements, it is indicated that the most of oxidized large molecules is the humic acid. According to the Zeta potential measurement, the chlorine dioxide is play as the coagulant aid to decrease the amount of THMFP and the formation of ClO_2^- and ClO_3^- with the low pH condition.

RB20

COMBINED UV LIGHT AND CHLORINE DISINFECTION OF RECLAIMED WATER: EFFECTS ON CORROSION AND WATER QUALITY WITHIN DISTRIBUTION SYSTEMS

Wang Haibo*, Hu Chun*, Hu Xuexiang, Yang Min, Qu Jiuhui

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 10085, China

wanghaibo_wang@126.com; huchun@rcees.ac.cn

The effects of sequential ultraviolet (UV) and chlorine disinfection on reclaimed water quality stability were assessed in a model reclaimed water distribution system (RWDS) using annular reactors (ARs).

UV irradiation not only enhanced the inactivation of heterotrophic bacteria, but also reduced the required initial chlorine dose, on the basis of heterotrophic plate count (HPC) analysis and chlorine consumption under different conditions. Moreover, UV pretreatment decreased iron release and turbidity of effluents resulted from Larson-Skold Index (LI) of reclaimed water changing, enhancing the stability of water quality through RWDS. Fourier transform infrared spectroscopy and high performance size exclusion chromatography measurements showed that the phenolic O-H stretching and the antisymmetric C=O stretching of quinones for dissolved organic carbon (DOC) in reclaimed water were eliminated by 60 mJ/cm^2 UV treatment, reducing the reactivity of DOC with chlorine.

Moreover, the corrosion bacteria within the biofilm on the corrosion scales could grow selectively with different disinfection processes. In the AR with combined UV and chlorine treatment, the iron-oxidizing bacterium (IOB) *Acidovorax defluvii* and the iron-reducing bacteria (IRB) uncultured *Rhodoferax sp.* and uncultured *Geobacter sp.* appeared on the biofilm. In contrast, in the AR treated with chlorine alone, the IOB *Sediminibacterium salmoneum* and the IRB uncultured *Geobacter sp.* were predominant in the biofilm. In the latter, *S. salmoneum* respiration predominantly contributed to the oxidization of Fe(II), whereas in the former, either Fe(II) or acetate acted as a donor for *A. defluvii* respiration, causing an increased depletion of oxygen by the oxidation of Fe(II). Therefore, under the former conditions, the composition of corrosion bacteria could result in higher corrosion inhibition, decreasing the effect of LI changes on corrosion.

All results indicated that UV irradiation enhanced water quality stability in the RWDS by inactivating bacteria and changing the structure of DOC in the reclaimed water.

RB21

DEVELOPMENT OF AN *IN SITU* REMEDIATION TECHNOLOGY FOR BTEX-CONTAMINATED GROUNDWATER BY THE USE OF IRON OXIDE NANOPARTICLES

Meyer C. [1], Bosch J.[1], Meyer A.[2], Pilloni G.[1], Fritsche A.[3], Höss S.[4], Meckenstock R.[1]

[1] Helmholtz Zentrum München, Institute of Groundwater Ecology, Neuherberg, Germany
[2] Isodetect GmbH, Neuherberg, Germany
[3] Friedrich-Schiller University Jena, Institute of Geosciences, Jena, Germany
[4] ECOSSA, Starnberg, Germany

carolin.meyer@helmholtz-muenchen.de

Microbial reduction of ferric iron is a major biogeochemical process in groundwater ecosystems and often associated with the degradation of organic contaminants. There, bacteria couple iron reduction to the oxidation of organic molecules, whereby carbon dioxide is produced. However, ferric iron in natural iron oxide minerals is poorly soluble, shows a high crystallinity and is thus hardly bioavailable for microorganisms. However, environmental nanosized iron(oxy)hydroxide minerals seem to have an enhanced reactivity compared to bulk materials of the same mineral class [1]. The same could be shown for synthetic iron(oxy)hydroxide minerals, produced in the laboratory [2].

In a new approach, we want to use this high reactivity of colloidal iron(oxy)hydroxides for a new remediation technology for BTEX-polluted groundwater horizons. Our aim is to produce reactive iron oxide colloids, which can be injected into a contaminant plume in order to stimulate the microbial iron reduction and degradation of contaminants. Because of a controllable release of colloidal iron oxide particles to the groundwater, by an adjustment of the salt concentration, we are able to create a strong reactive barrier within the contaminant plume.

Therefore we examined the reactivity of nanosized, synthetic colloidal iron(oxy)hydroxides in microbial iron reduction in batch incubations and column experiments. First studies on the feasibility of this technology showed an about 5-fold enhancement of toluene oxidation after application of nanosized iron oxide particles to microbial incubations. Furthermore, soil column experiments demonstrated the high persistence of nanosized iron oxides under simulated environmental conditions, opening the perspective for their technological application as electron acceptors in the remediation of BTEX and putatively PAH contaminated sites. Additionally, ecotoxicological analyses with relevant organisms demonstrated no perturbing effect of colloidal iron(oxy)hydroxides in relevant concentrations.

Our results suggest that the injection of ferric iron nanoparticles as electron acceptors for microbial contaminant degradation in contaminated aquifers might develop into a novel bioremediation strategy creating in situ reactive barriers. In a targeted approach, we will be able to create sustained zones of enhanced biological activity, which will consume all passing contaminants.

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RB22

ELECTROREMEDIATION OF DRILLING MUDS USING FACILITATING AGENTS

Boulakradache M.O.[1], Akretche D.E.[1]*, Yassaa N.[2],Ait-Idir A.[3] and Cameselle C.[4]

[1]Laboratory of Hydrometallurgy and Molecular Inorganic Chemistry, Faculty of Chemistry, University of Science and Technology Houari Boumediene,USTHB, B.P. 32 El – Alia, 16111 Bab – Ezzouar, Algeria
[2]Laboratory of Functional Organic Analysis, Faculty of Chemistry, University of Science and Technology Houari Boumediene,USTHB, B.P. 32 El – Alia, 16111 Bab – Ezzouar, Algeria
[3]Entreprise Nationale des services aux puits (ENSP), Hassi-Messaoud, Ouargla, Algeria
[4]Laboratory of Bioprocesses, Dept of Chemical Engineering, University of Vigo. University Campus. Building Fundacion, 36310 - Vigo. Spain

dakretche@hotmail.com or dakretche@usthb.dz

Drilling mud sited in the south of Algeria give rise to an important pollution due to the presence of hydrocarbons and PAH'S. The remediation of these components is more difficult regarding the various species which exist and the interactions which occur between them. In this work, after the analysis of a sample of a real drilling mud, electrokinetic remediations of simulated samples have been tested. Knowing that hydrocarbons are hydrophobic, facilitated agents are added i.e. surfactants and co-solvents. Oxidants have also been added to test their ability to reduce the toxicity of some components by their reduction.

Electrokinetic tests were carried out in a cylindrical cell in Glass where the central compartment of 1 liter (inner diameter = 2.5 cm) containing 300 grams of a simulated drilling mud is separated from cathodic and anodic sides by a filter paper (Whatman N°5) inserted between a grid of rigid nylon (mesh size = 2mm) and fibers ion exchange FIBAN A6 OH^- form and Fiban $K1H^+$ form or ion exchange membranes. The circulation of the catholyte and the anolyte is ensured by a peristaltic pump (Watson Marlow 313S) from graduated reservoirs (250 ml each) at a flow rate of 15 $ml.mn^{-1}$ which allows the escape of generated gas near the electrodes. In the two extremities there are two graphite electrodes. The variation of the composition of the sample is followed by analyses using Infrared spectroscopy, Gas Chromatography coupled to Mass Spectra and UV spectroscopy. 200 to 1000 ppm of zinc are added to the clay and their removing is followed. The applied voltage is delivered by a power supply and maintained constant in all the runs.

The influence of some parameters is examined as current density, pH and conductivity. The role of the concentration of facilitating agent is also shown and the various results obtained are discussed and allow a solution for the treatment of drilling mud.

RB23

EVALUATING CHINA'S BC EMISSION INVENTORY USING BC TO CO RATIOS: INTEGRATED ANALYSIS OF *IN SITU* OBSERVATIONS AND MODELING

Wang Yuxuan[1]*, Wang Xuan[1], Kondo Yutaka[2], Kajino Mizuo[3], Munger J. William[4], Hao Jiming[1]

[1] Center for Earth System Science and School of Environment, Tsinghua University, Beijing, China
[2] Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo, Japan
[3] Meteorological Research Institute, Tsukuba, Japan
[4] Department of Earth and Planetary Sciences and School of Engineering and Applied Sciences. Harvard University, Cambridge, Massachusetts, USA

yxw@tsinghua.edu.cn

Ambient-measured BC/CO ratios offer additional constraints to evaluate BC emissions as the ratios differ by combustion type and condition, but the influence of atmospheric processes, particularly wet deposition, needs be quantified. In this study, we use the observed mass concentrations of BC and their correlations with CO at Miyun, a rural site near Beijing, during the non-heating seasons of 2010 (April to October), to constrain BC emission estimate for North China Plain (NCP) through a 3-D chemical transport model (GEOS-Chem). BC has moderate to strong positive correlations with CO (R2=0.51) at the site. The model captures the observed temporal variability of BC (R = 0.7), but underestimates BC concentrations by 22%. The rate of decrease of the BC/CO ratio with increasing precipitation is about a factor of two slower in the model than in the observations, suggesting the need of more efficient wet removal process of BC in the model. We estimate that wet removal contributes to a positive bias of +19% in simulating BC concentrations, while the model's resolution introduces a negative bias of -11%. After quantifying these two types of model biases, we estimate that the bottom-up inventory of Zhang et al. [1] used in the model underestimates BC emissions from NCP by about 33%. The difference is most likely to be attributed to the industry or transportation sector.

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RB24

MICROBIAL APPROACH : AN AID TO ENVIRONMENT REGENERATION – A CASE STUDY FROM INDIA

Sharma S. K.

Head, Department of Environmental Education, Carman Residential and Day School, Dehradun 248007, India

SKS105@rediffmail.com

Increasing ecological awareness of protection of environment has focused the attention of global scientists towards the oil pollution problems. One of the problems is reclaiming the oil affected sites. This problem is being tackled by old faithful clean up method such as land fills, aeration procedures or removing the top soil. Later on thermal and chemical treatment methods were also used. But these treatments are expensive and require the use of air emissions control devices and continuous air monitoring. Therefore, more stringent restrictions pertaining to oil pollution and increasing cost associated with traditional technologies have lead to the development of bioremediation technique. A breakthrough has been achieved in developing an indigenous bioremediation technique to tackle he crude oil polluted sites by developing a population of microorganisms capable of biotransformation of contaminants by isolating and amplifying the capabilities of crude oil specific biodegrading microorganisms and defining the appropriate nutrient chemistry and physicochemical environmental parameters in order to optimize bioremedial performance. A culture medium is developed for the reduction in bactericide evaluation period. The use of this medium for bactericide evaluation against Sulfate Reducing Bacteria (SRB) has reduced the evaluation period from 28 days to 10 days. It is found to be cost effective as compared to other remediation methods and consequently, leads to the degradation of pollutant to environmentally benign end products of CO_2 and H_2O. It greatly reduces the liability of generating end products needing disposal and fixation, which do not result in the ultimate destruction of the contaminants.

The following figures shows the in- situ bioremediation of oil soaked soil.

Oil affected site before Bioremediation

Same site after the Bioremediation treatment

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RB25

CATALYTIC OXIDATION OF O-XYLENE OVER PALLIDIUM SUPPORTED ON Co_3O_4 CATALYST

Wang Yafei, Zhang Changbin, Yu Yunbo, He Hong*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085,
PR China

honghe@rcees.ac.cn

Volatile organic compounds (VOCs) are harmful to human health and the environment. Benzene, toluene and xylene (BTX) are one kind of the major VOCs in air in a large scale. Catalytic oxidation is considered to be the most suitable pathway for the removal of VOCs owing to its easy application, high efficiency and low production of thermal NOx [1]

In this study, mesoporous Co_3O_4(3D) was prepared by a nanocasting route using mesoporous KIT-6 silica [2] as a hard template and tested for the total oxidation of oxylene in the temperature range of 150~300°C. The mesoporous Co_3O_4 (3D) exhibited a much higher activity than the Co_3O_4 (P) catalyst synthesized by precipitation method [3]. The Pd addition further improved the catalytic activity of the mesoporous Co_3O_4(3D) and 90% conversion of 150 ppm o-xylene can be achieved at 246°C over the Pd/Co_3O_4 (3D) catalyst at a space velocity of 60,000 $mL \cdot g^{-1} \cdot h^{-1}$. The prepared materials were characterized by BET, XRD, TEM, XPS and H2-TPR methods. The BET and TEM results indicate that the mesoporous materials have uniform channel dimensions. The TPR and XPS data indicate that Pd was well dispersed on the surface of Co_3O_4 (3D) and could easily activate the oxygen. Therefore, Pd/Co_3O_4 (3D) showed the highest activity for catalytic oxidation of o-xylene among four catalysts.

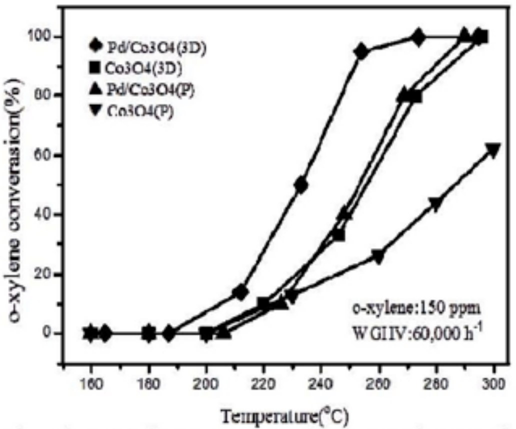

Fig. 1. o-Xylene conversions on the catalysts

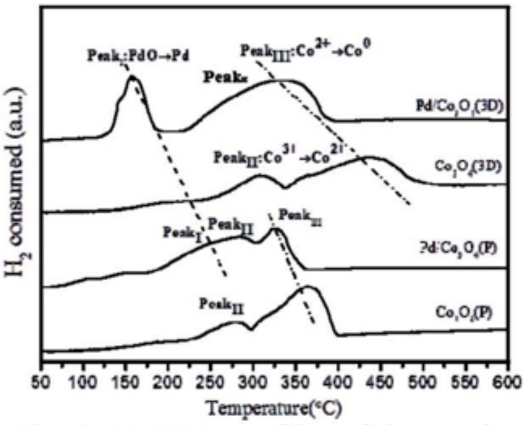

Fig. 2. H_2-TPR profiles of the catalysts

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PB1

MOBILE INFRASTRUCTURE IN A AGRICULTURAL PRODUCTION

Traballi Rogerio, Traballi Amanda G. M., Queiroz Alexandre, Roberto Ramos Carlos, Leme Ednilse , Duarte Leandro Juliana, Hellmeister Pedrosa Ylara

1 Universidade Paulista - UNIP

rogeriotraballi@me.com

Key Words: Agricultural, production, Brazil, Mobile

Agricultural production when you see its system of storage, distribution and logistic as a whole but the final price represent much of infrastructure,distribution and logistic in Brasil.

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PB2

DECOLORIZATION-DEGRADATION OF THE AZO DYE ORANGE G VIA HETEROGENEOUS FENTON REACTION BY WASTE ZINC BEARING MAGNETITE COMPARED WITH SYNTHESIZED MAGNETITE

Wu Honghai,[1,2]* Chen Xiaoling,[1,2] Li Yilong,[1,2] Li Guotian,[1,2] Liu Yifan

[1] School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China.
[2] Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou 510006, PR China

whh302@163.com

Environmentally friendly iron-bearing minerals such as magnetite and goethite as heterogeneous Fenton catalysts in the degradation of the dyes and pesticides have been paid attention due to their proven and excellent catalytic reactivity towards H_2O_2 [1, 2]. In the present study, decolourization-degradation of the azo dye Orange G (OG) was investigated in detail by using industrial waste zinc-bearing magnetite (WMT) and synthesized magnetite (SMT)/H_2O_2 as heterogeneous Fenton-like reagents under dark and visible irradiation. Magnetite surfaces catalysed a Fenton-like reaction responsible for decolourization-degradation of OG following pseudo-first order kinetics (R2>0.97). These processes were effective but seriously impacted by the medium pH values and the dosages of both the different magnetite catalysts and H_2O_2. The decolourization- degradation efficiencies of OG increased with the decrease of solution pH and/or the increase of H_2O_2. The acidic aqueous medium conditions were likely favourable due to the enhanced surface adsorption of the negatively charged azo dye OG leading to the promotion of decolourizing-degrading OG. However, the effect of zinc substitution in the WMT on the decolourization-degradation efficiencies of the dye OG was relatively obvious under visible irradiation compared with dark irradiation. On the other hand, due to its large specific surface area the WMT displayed significantly higher oxidative decolourization-degradation efficiencies (TOC) of OG for comparison with the SMT. This implied that between decolourization and degradation of OG were not completely uniform during the Fenton-like reactions. In addition, the zinc substitution alike ZnO may partially contribute to the OG degradation by photo-catalyzation, but did not play the role of the transition metals Co^{2+}, Mn^{2+}, V^{3+} and Cr^{3+} at the octahedral sites that could decompose H_2O_2 to produce •OH and accelerate the electron transfer [2, 3].

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PB3

DOES CLIMATE CHANGE A THREAT TO URBAN GOVERNANCE IN BANGLADESH? AN OVERVIEW ON DHAKA MEGA-CITY

Shafiqul Alam SM

Department of Management Studies, School of Management, University of Tampere, Tampere, 33014, Finland

sm.alam@uta.fi

Cities in developing countries are at particular risk of the impact of climate change. Dhaka, the capital of Bangladesh, is a largest and densely packed megacity in the world. Due to the over population, critical geographic location, unplanned human and industrial settlement, unplanned land use and infrastructural settings and environmental degradation, Dhaka has become an extreme vulnerable megacity to climate change in the Asia and World as well. On the other hand, due to increase of industrialization, electricity consumption and motor vehicle use, generation of greenhouse gases (GHG) and air pollution of Dhaka is now in danger level. Moreover, Dhaka is most vulnerable flood prone city both from the rivers and rainfall that beyond the capacity of the city. The governance and management of Dhaka City are under a multiple organizational jurisdictions, where as many as 40 institutions are involved. In practice, governance of Dhaka megacity has become complex due to the multiplicity and lack of coordination among its agents. Consequently, Dhaka city dwellers have been facing multifarious environmental problems. These problems intensified the climatic problem of the city. Failing to address the climate change impact will be a great hindrance to economic development and existence of city in the long-run. In this circumstance, this paper discussed the practical scenario of climate change impacts in Dhaka and existing policies, adaptations and mitigation programs taken in the city to face climatic problems. The paper has been prepared based on the secondary and primary sources of data. The results of the paper revealed that the Dhaka is most vulnerable with widespread impacts of climate change and there are no comprehensive and integrated efforts in urban governance of Dhaka to address the existing threats and challenges of climate change in future. However, few policy guidelines and initiatives for adaptation and mitigation programs on climate change impact found separately by various agents of urban governance in Dhaka. The paper recommends integrated urban climate governance for adaptation and mitigation of climate change challenges in Dhaka Mega-City.

PB4

ENHANCED ELECTROKINETIC REMEDIATION OF HEAVY METALS AND PAHS FROM DREDGED MARINE SEDIMENT

Ammami M.T.[1,2]*, Portet-Koltalo F.[1] , Benamar A.[2],Wang H.[2]

[1]UMR 6014 COBRA, Université de Rouen, 55 rue Saint Germain, 27000 Evreux, France.
[2]Laboratoire Ondes et Milieux Complexes, UMR 6294 CNRS, Université du Havre, 53 rue de Prony, 76600 le Havre, France.

mohamed-tahar.ammami@univ-lehavre.fr

Sediments are dredged from harbors and channels to maintain navigational depths. However harbor sediments are generally contaminated by organic and inorganic contaminants. Little contaminated sediments are typically disposed of at sea but highly contaminated sediments are rather disposed of in lagoons, at land or in confined disposal facilities and reuse solutions can be proposed if they are treated before. Electrokinetic (EK) remediation can be a promising treatment for the removal of cationic heavy metals from low-permeable matrices such as sediments but is limited for PAHs which are nonionic and have a low aqueous solubility.

In our study, electrokinetic experiments were conducted under a constant potential gradient ($1V.cm^{-1}$) with various processing fluids to improve the decontamination of artificially contaminated sediments with heavy metals (Cd, Cr, Cu, Pb and Zn) and five PAHs. Results revealed that adding a strong inorganic acid (nitric acid) into the aqueous fluid was more effective than adding a weak acid (citric acid) to remove heavy metals from the sediment, but the complexing citric acid was promising for longer treatments.

Concerning PAHs, an anionic surfactant (sodium dodecyl sulfate SDS) and a nonionic surfactant (Tween 20) were tested to mobilize, solubilize and favor their EK migration. In all experiments, the low weight PAH (phenanthrene) was better extracted than the other PAHs. But using simultaneously SDS and citric acid or Tween 20 and citric acid improved the extraction of high weight PAHs, because the electro-osmotic flow was higher with the mixture surfactant + acid than when surfactant was used without acidification of the medium. Thus EK treatment with a combination of a surfactant and citric acid was the most effective to extract simultaneously PAHs and heavy metals. Consequently, this mixture was also tested on real dredged sediments from a Norman harbour disposal site.

ADSORPTION OF PESTICIDE AND PHARMACEUTICAL COMPOUNDS ON NATURAL POROUS MINERALS

Ansanay-Alex Salomé [1], Soulier Coralie [2], Lomenech Claire [1], Hurel Charlotte [1], Marmier Nicolas[1*]
and Budzinski Hélène[2]

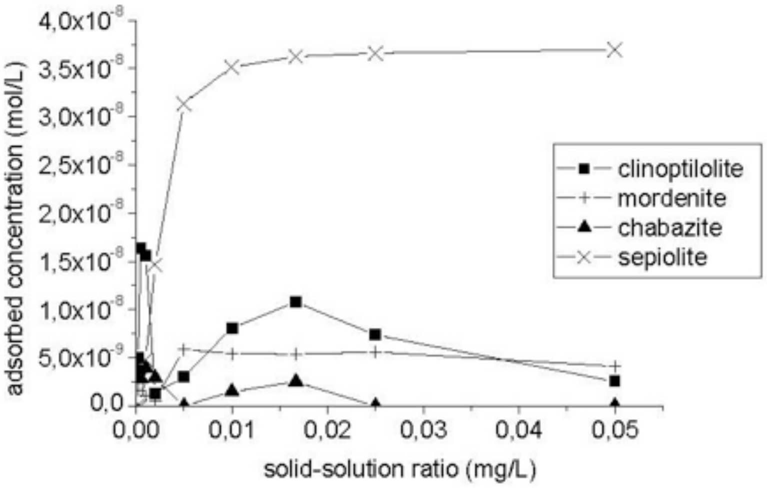
[1]University of Nice Sophia Antipolis, ECOMERS, Parc Valrose, 28 avenue Valrose, 06108 Nice cedex 2, France
[2]University Bordeaux 1, EPOC-LPTC, UMR CNRS 5805, 351 Cours de la Libération, 33405 Talence Cedex, France

Nicolas.Marmier@unice.fr

Since the European Union has adopted the Water Framework Directive (WFD) in October 2000, the quality of water environment has become a priority for its different members who are obliged to reduce or remove the different toxic substances contained in the aquatic environment. In this context, we were interested by common organic contaminants like pesticides and pharmaceuticals, and by the use of natural porous materials as adsorbents to remove these contaminants from water.

In this way, three natural zeolites (clinoptilolite, mordenite, chabazite) and one clay (sepiolite) were selected as potential adsorbents. The adsorption capacity of these solids for different pharmaceuticals and pesticides was investigated using batch method developed by the Environmental Protection Agency (EPA)[1].

The adsorptions of 10 µg/L of Linuron (pesticide) onto the four selected adsorbents as a function of the solid-solution ratio at pH = 7.0 ± 0.1, $I = 10^{-2}$ $mol.L^{-1}$ (NaCl) are presented in the next figure.



The results showed that sepiolite is the only solid presenting a normal profile of adsorption, which increases with increasing solid-solution ratio. This difference of adsorption profile between sepiolite and zeolites can be explained by a greater adsorption efficiency of sepiolite.

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PB6

EFFECT OF FILLING MEDIA ON THE PERFORMANCE OF TRICKLING FILTERS USED FOR THE TREATMENT OF MUNICIPAL WASTE WATER

Bash Al-Malikey Salam J., [1]*, Zardawi Mustafa I.[2]

[1] College of Engineering, AlMustansiriya University
[2] Mayoralty of Baghdad

bashs@ohio.edu or salambash2000@yahoo.com

A trickling filter model with three different filling media (Wild Thorn, Arum Plant (Fiber) and Palm Tree Bark), was made for biological treatment of municipal waste water. This is the first documented attempt, on the international level, of using these plants as fillings for the trickling filters. The tests were run for three different superficial flow rates (15, 30 and 45 $m^3/m^2.d$) without recycling. The operation of the model was continuous for about four months, so as to consider the variation in ambient temperature. Results indicate that good BOD5 removal efficiencies may be gained by the use of these filling Medias. With a superficial flow rate of (15 $m^3/m^2.d$), efficiencies of about (76%, 71% and 62%) for Wild thorns, Arum Plant (Fiber) and Palm tree Bark, respectively, were achieved under ambient temperatures of about 36-40° C, and (73%, 69% and 61%), in the same manner, under 23-25° C. A problem of filter clog was indicated with the use of Palm tree Bark under high superficial flow rates (above 30 $m^3/m^2.d$). In addition to that, it was noticed a high abundance of flies around the trickling filter model with the use of all tested filling media.

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PB7

STUDY OF METHYLEN BLUE ADSORPTION ON THE ALGERIAN PALYGORSKITE

Youcef L.Dali[1], Belaroui L.S. [1,2*], Bengueddach A.[1]

[1]LCM, Faculté des Sciences, Université d'Oran, BP 1524 Oran El M'Naouer, Algérie.
[2]Département de Pharmacie, Faculté de Médecine, Université d'Oran, BP 1510 Oran El M'Naouer, Algérie.

lalasettibelaroui@yahoo.fr

Clays are natural minerals which are spread throughout the Algerian soil. In the two last years, a new clay mineral was discovered named Attapulgite. This material is fibrous clay of palygorskite's family, formed of an octahedral layer sandwiched between two tetrahedral layers, resulting in a discontinuous sequence with the presence of canals. Our study is about the adsorption of cationic dye methylen Blue by the Algerian attapulgite noted Atta@dz.

In the first time, our material is characterized by the usual methods of analysis like the infrarouge spectroscopy (FTIR), the X ray diffraction (XRD) and the chemical analysis.The results give the following chemical composition: SiO_2-37.93; Al_2O_3-8.41; MgO-7.92; Fe_2O_3-6.09; CaO-15.59, a specific surface area of 80 $m^2.g^{-1}$ and the Xray diffraction revealed the presence of the first ray at 10,27Å.

After that, the kinetic study of this adsorption reaction is realized. This reaction is followed by UV Visible spectroscopy that allows determining the optimal parameters of adsorption with a fixation pourcentage of 97% after 5 minutes of reaction. The adsorption isotherms' modelisation, demonstrated that the adsorption of methylen blue in this palygorskite follows the Langmuir model with a maximum adsorption capacity about 57,47 $mg.g^{-1}$. The kinetic and thermodynamic study of this reaction enable us to conclude that the adsorption of the cationic dye in the fibrous clay is an endothermic reaction of the second pseudo order with a kinetic constant of about 0,203.

PB8

CHOICE OF AN ADSORBENT FOR GLYPHOSATE IMMOBILIZATION AND BIODEGRADATION – PHYSICAL CHEMICAL PROPERTIES

Arraj T.[1]*,Bersillon J.L.[1], Echevarria G.[2], Kara Ali A.[3]

[1]LEM, l'Ecole Nationale Supérieure de Géologie (ENSG), INPL, Nancy, France.
[2]LSE, ENSAIA, l'Institut National Polytechnique de Lorraine (INPL), Nancy, France.
[3]Department of Marine Chemistry, Higher Institute of Marine Research, Tishreen University,
Latakia, Syria.

tareq.arraj@univ-lorraine.fr

Glyphosate (N-(phosphonomethyl) glycine) is a post-emergent, systemic and non-selective herbicide that is used in both agricultural and non-agricultural areas all over the world. Its increasing use requires special attention to its transfer from terrestrial to aquatic environments. The aim of this project is to remove the glyphosate contained in agricultural drainage water by adsorption and biodegradation in a constructed wetland. Therefore, several objectives are sought: (i) select a suitable sorbent for preliminary retention of glyphosate, (ii) select a plant that will support rhizosphere microbial activity which will degrade glyphosate, and (iii) optimize agronomic practices on a full-scale constructed wetland using the sorbent and the plant.

The intended process is to biodegrade glyphosate previously adsorbed on a substrate. This substrate must fulfill 2 purposes: (i) be a good adsorbent for glyphosate and (ii) not hinder the development of rhizosphere associated to the managed wetland vegetation. Based on previous works concerning phosphate and arsenic removal on one hand and glyphosate behavior in soils on the other, 2 supporting materials were investigated for their ability to adsorb phosphate:

- The Bauxaline® (Rio Tinto - Alcan, Gardanne, France), which is a byproduct of the aluminum industry.
- The GEH 104® (GEH Wasserchemie, Osnabruck, RFA), which is a highly efficient adsorbent whose operating principle is based on the chemistry of ferric hydroxide.

Complete characterization of both media was performed through elemental analyses, X-Ray diffraction, infrared spectroscopy, specific surface area (BET), electron microscopy (SEM and TEM) and phosphate adsorption behavior. GEH 104 was found to be best as a support as it displays a much higher surface area, greater affinity for phosphate and less impurities than Bauxaline and was further exposed to glyphosate solutions.

The next step will consist in cultivation trials of plants that were previously screened to grow sufficiently in such environments (i.e. Phragmites and Salicaria) at laboratory scale in order to optimize agronomical procedures with the final goal of decaying glyphosate. The last step will be the implementation of this technique (support and plants) on a cultivated watershed in order to validate the process at field scale and to evaluate performances and economics of such a treatment of agricultural drainage.

PB9

DETERMINING LEVEL OF DAMAGED ECOSYSTEMS OF CASPEAN SEA AREA

Kenzhyn Zh., Rakhmanova Zh.[1], Sagynbaev S. O.[2], Bekturganova A.D.[2], Bigalyeva R.K.[3], Zhanburshin E.T. [2 1,]
Bigalyev A.B.*

Al Faraby Kazakh National University,Almaty[1] , Department of natural resources protection and using of Mangystau district,
Aktau twn[2], Asphendijarov Kazakh National Medical University, Almaty c.

aitkhazha@gmail.com

In the short term development of oil and gas deposits on the continental shelf of the Caspian (Kashagan) may dramatically increase the environmental burden not only on the Kazakhstan part of Caspian Sea region [1,2], but throughout the waters of the central and northern part of the Caspian Sea. One of the most common and dangerous for biota associated petroleum contaminants are heavy metals, which is polluted at the same time as the water environment and soils of the coastal zone. Devising a successful phytoremediation strategy necessitates selecting plants with enhanced tolerance to metals and metal hyper accumulation (inclusive of uptake, translocation and sequestration) [3,4]. It is well established that all higher plants can accumulate heavy metals in different concentrations. However, significant differences in metal accumulation were shown between and within plant populations. There are an indications in the literature that amaranth plant species may accumulate heavy metals in their organs [5,6]. Since in Kazakhstan the populations of two amaranth subspecies A. paniculatus and A.tricolor are widespread and Cd, Cu and Zn are more important pollutants in the industrial regions, further experiments were carried out with these heavy metals using the Kazakh populations of these two amaranth subspecies. We studied therefore the effects of increased concentrations Cu, Cd and Zn on the growth and development of the subspecies of amaranth [7 Bigaliev a.oth., 2003]. Growth rate and biomass production of amaranth plants were used for determination of the toxic levels of heavy metals. Source removal technologies full or particle excavation, if possible larger unsaturated zones: first – step wize up-scaling to full remedition, second - extrapolate within each cluster.

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PB10

FE/P/S INTERFACE AS ANODE IN MICROBIAL FUEL CELL FOR THE TREATMENT OF WASTEWATER

Bouabdalaoui L.[1]*, Legrand L.[1], Feron D.[1, 2], Chaussé A.[1]

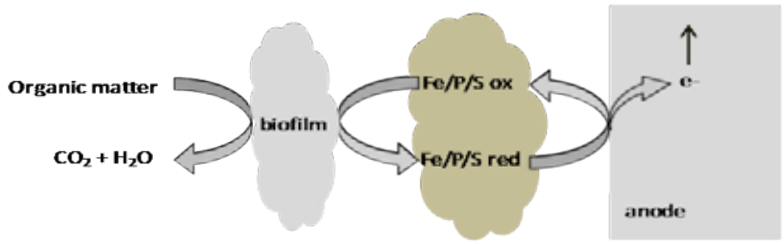
[1]LAMBE Université d'Evry, Bd François Mitterrand, 91025 Evry Cedex, France
[2] Service de Corrosion et du Comportement des Matériaux dans leur Environnement, CEA Saclay, Bât.458, 91191 GIF-SUR-YVETTE, France

bouabdalaoui.laila@gmail.com

Microbial fuel cells (MFC) are electrochemical devices that use the metabolic activity of microorganisms to oxidize organic matter (fuels) and produce electrons that are collected at the anode and transported to the cathode through an external circuit. Various sources of organic matter including biomass, domestic or industrial wastewaters can be used as fuels in anodic compartment. MFCs can then allow both water treatment and electricity generation.

Graphite is commonly used as anode material, Dumas et al. [1]. The electrons can be transferred directly to the anode (microorganisms in anode biofilm) or indirectly (electron chemical shuttles) Z.Du et al. [2] and K. Watanabe et al. [3]. In the first case, it is often necessary to wait for several weeks before the formation of efficient biofilm. We have developed catalytic interfaces that do not require any significant starting delay and that display higher current performances, as compared to pure graphite. The electroactive compounds are mixed Fe/P/S solids obtained from coprecipitation onto graphite suspension of Fe^{2+} and HS^- ions in phosphate buffer solution. These solids were characterized by FTIR, SEM, XRD and µRaman. For the fabrication of anodes, Fe/P/S-modified graphite particles are fixed to a stainless steel disc with the aim of carbon ink. The anode is installed at the bottom part of a 5x5 cm square home-made MFC with about one centimeter height anodic compartment filled with 1 mM NaCl / garden compost solution while the cathode, made with a stainless steel grid is at the top of the device.

MFC voltage values were recorded as a function of storage time. Within the first two days, the anode potential decreases from about -0.35 to -0.6V/AgCl/Ag and then stabilizes, mainly indicating that a biofilm rapidly forms and that $(Fe/P/S)_{ox}$ formed during air exposition can be reduced back to $(Fe/P/S)_{red}$ from anaerobic bacteria activity in anodic compartment. A similar reactivation is also obtained after each discharge step. From periodic discharge experiments, we obtained current-voltage and power density features. The influences of anode parameters (surface, Fe/P/S composition, operating temperature…) were studied. A maximal power density of ~10 $W.m^{-3}$ at a current density of ~25 A/m^3 was obtained. Under these operating conditions, the treatment of 1 m^3 of 200 $mg.L^{-1}$ COD wastewater would theoretically last for about 27 h and would produce an electrical energy of 270 Wh.



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PB11

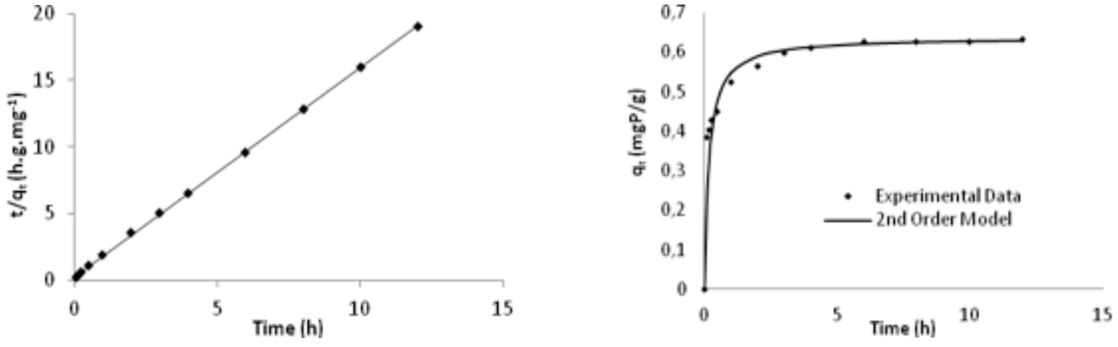
ADSORPTION OF PHOSPHATE BY LATERITE AND SANDSTONE FROM IVORY COAST: ABSORBENT DOSE EFFECT AND KINETIC

Coulibaly L. S.[1,2,3]* , Coulibaly L.[3,] Yvon J.[1]

[1] Laboratoire Environnement et Minéralurgie, UMR 7569 CNRS-INPL, 15 Avenue du Charmois, B.P. 40. F-54501, Vandoeuvre-Lès-Nancy Cedex
[2] Laboratoire Géosciences et Environnement, 02 B.P. 802 Abidjan 02
[3] Laboratoire Environnement et Biologie Aquatique, 02 B.P. 802 Abidjan 02

sandotin.coulibaly@ensg.inpl-nancy.fr

The link between eutrophication and phosphate, essentially from wastewater, is well established [1]. The reduction of phosphates in wastewater before the rejection in the environment is of interest to slow down eutrophication. Several phosphorus-removal technologies are available, involving metallic salts of iron, aluminum and calcium precipitation, and some organo-cationic polymers [2]. There are also some solutions using assimilation of phosphates by bacteria and plants in the biological process [3]. However, difficulties of manipulation, large amounts of chemical sludge produced and operating costs are obstacles in the use of these techniques [4]. In particular, for developing countries, environmental issues required specific treatment processes that can be readily available and costly affordable. This study assesses the capacity of natural laterite and sandstone from Ivory Coast as potential phosphate-removing substrate in batch tests. The characterization of laterite and sandstone indicates that they mainly contain very high levels of iron and aluminum oxy-hydroxides and diverse dioctahedral clays. This mineralogical composition is concordant with a potential phosphate adsorption capacity of interest for these materials. Phosphate adsorption tests were carried out using crushed laterite and sandstone (250 µm) with specific surface areas of 34.1 ± 0.4 and 4.7 ± 0.6 $m^2.g^{-1}$ respectively. Optimal doses and effects of pH on adsorption were analyzed from phosphate solution of 10 $mg.L^{-1}$ at 30±2°C. Effect of initial concentrations (1; 5 and 10 $mg.L^{-1}$) on the adsorption kinetics was studied for 24 hours. The variations of adsorbent masses lead to an optimal dosage of 15 and 20 mg/L respectively for laterite and sandstone. Adsorption data were modeled using the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics equations. Among these models, the pseudo-second-order equation successfully described the kinetics of the phosphate adsorption on these adsorbents. The rates constants (k2) were 9.75 $g.mg^{-1}.h^{-1}$ and 261.71 $g.mg^{-1}.h^{-1}$ with equilibrium time of 6 hours and 4 hours respectively for the laterite and the sandstone. These results indicate that these laterite and sandstone can beneficially be used for the removal of phosphate from wastewater.



Plots of sorbed capacity versus time for sorption kinetics of phosphate on laterite at 30°C, pH=6,5; [P]=10$mg.L^{-1}$.

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PB12

ORDERED MESOPOROUS ORGANOSILICAS AS SORBENTS OF HEAVY METAL IONS

Dąbrowski A.[1], Barczak M.[1]*, Lata L.[2], Bartmiński P.[2]

[1]Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20 031 Lublin, POLAND
[2] Faculty of Earth Sciences and Spatial Management, Maria Curie-Sklodowska University Al. Kraśnicka 2, 20-718 Lublin, POLAND

mbarczak@poczta.umcs.lublin.pl

Ordered mesoporous organosilicas (OMOs) represent broad class of porous materials [1-3]. High values of specific surface areas, large pore volumes and diverse morphologies make them very attractive materials in the fields related to catalysis, adsorption, water remediation etc. [4-8]. An important advantage of the sol-gel synthesis of OMOs is the possibility of introduction of the organic groups into the ordered structure during one-pot synthesis [9-11]. Thus, proper choice of organic functionalities introduced into the framework can result in creation of effective and selective sorbents for heavy metal ions.

In this work SBA-15 and SBA-16 materials functionalized with different groups were synthesized and characterized by FT-IR spectroscopy, powder X-ray diffraction, thermogravimetry, transmission electron microscopy and nitrogen sorption measurements. The resulted materials exhibited well-ordered mesoporous structure, high values of surface area and high contents of functionalities introduced by cocondensation of the monomers. Selected samples have been tested as sorbents of Hg^{2+}, Pb^{2+}, and Cd^{2+} ions from liquid phase. Observed static sorption capacities testify to great usefulness of these materials towards effective and selective removal of these ions from wastewaters.

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PB13

EFFICIENCY OF ARSENIC OXIDIZING BACTERIAL BIOFILMS FOR ARSENIC CONTAMINATED DRINKING WATER TREATMENT

Dictor M.C.,[1] Guezennec A.G.,[1] Lereau L.,[1] Deluchat V.[2], Simon S.[2], Michel C.,[1] C. Joulian C.[1]

[1] BRGM, Environment & Process Division - 3, av. Claude Guillemin - 45060 Orléans cedex 02, France
[2] GRESE, University of Limoges – 123 av Albert Thomas – 87060 Limoges Cedex

mc.dictor@brgm.fr

In drinking water supplies, arsenic exists mostly as two inorganic forms, arsenite [As(III)] and arsenate [As(V)] which are toxic to living organisms [1]. According to WHO recommendations, the drinking water standard was reduced from 50 to 10 µg/L and many regulatory agencies have recently accepted this new standard [2]. Most of the existing treatment processes are effective only on arsenic anionic forms [As(V)] and not on neutral and mobile arsenic complexes [3]. To overcome this lack of efficiency, a first oxidation step of As(III) form is necessary and is usually performed using strong oxidant or binding materials that are costly for small drinking water treatment units. An alternative to theses physico-chemical treatments is the biological treatment using As(III)-oxidising bacteria [4]. Numerous autotrophic bacteria are able to oxidise arsenic. Among them, *Thiomonas arsenivorans* [4-6] is able to oxidise As(III) up to 100 mg As(III)/L and appears to be a good candidate for its known capacity to use As(III) as an energy source and carbon dioxide or carbonates as carbon source. An As(III)-oxidizing biological treatment pilot unit coupled to trapping units for As(V) removal at the outflow of the biological bioreactor was performed on site in order to study the strength of the biological process in real operating conditions. The bioreactor was previously inoculated with the autotrophic As(III)-oxidizing *Thiomonas arsenivorans*. Then, it has been intermittently fed with contaminated water from the drinking water well, at site temperature (15-17°C) and under downstream mode. As(III)-oxidizing biofilm development has been followed during the pilot functioning using CE-SSCP-16S (targeting the global community) and PCR-DGGE-aoxB (targeting As(III) oxidizers) fingerprinting techniques. Results showed a complete colonization of the mineral support (*i.e.* pozzolana) by indigenous bacteria of the groundwater to be treated. Moreover, the oxidation yield of the biological step was in the range of 54 to 100 % depending on the residence time (from 30(?) to 7 minutes) and the residual As concentration at the end of the complete treatment process (biological oxidation and trapping) was below 2 µg As/L. These results are thus very encouraging for an industrial application in regard to the strength and its absence of nutrients supply, except for the low amount of oxygen needed if it is not in sufficient concentration in the site water.

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PB14

BIOSORPTION OF CR (VI) BY YEAST SUPPORTED ON GRANULAR POUZZOLAN IN FIXED-BED REACTOR

Djafer A.[1,2]*, Kouadri Moustefai S.[1], Idou A.[3], Azize A.[4]

[1] Laboratoire Eau et Environnement. Université Hassiba Benbouali Chlef , BP 151 - 02000 Chlef – Algérie
[2] Faculté des Sciences et Sciences de l'Ingénieur, Université Hassiba Benbouali Chlef
[3] Université des Sciences et de la Technologie Mohamed Boudiaf (USTO-MB), Bp. 1505 Bir El Djir, 31000 Oran,
[4] Laboratoire de Valorisation des Matériaux et Traitement des Nuisances, Université de Mostaganem, B.P. 227, Mostaganem 2000, Algérie

abddja72@yahoo.fr

Several industries in sectors such as tanning, metallurgy, surface treatment, etc., produce daily, huge amounts of wastewaters that are usually discharged untreated into the surrounding environment. The major pollutant containing in this liquid waste is chromium. Due to their hazardous characteristics and non-biodegradability, Cr (VI) generates extremely adverse problems to the environment and poses a great threat to human health. Then, it is of paramount importance to remove chromium from industrial effluents that are released to the main water bodies or to the land. The potential of immobilized yeast on granular pouzzolan to accumulate chromium as well as its biosorption capacity is investigated in this study in discontinuous mode. Variations of some parameters such as chromium solutions concentration, evolution pH, Time and Temperature, were considered to assess the fixed biomass performance. The experimental results indicate encouraging performance towards removal rates of 85–90%.The equilibrium uptake processes followed the first-order rate expression.

Keywords: Biosorption, yeast, hexavalent chromium, adsorption isotherms, biomass

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PB15

PREPARATION OF HIERARCHICALLY POROUS CARBON WITH HIGH ADSORPTION CAPABILITY BY USING DIATOMITE AS TEMPLATE AND CATALYST

Liu Dong[1], Yuan Peng[1]*, Tan Daoyong[1,2], Liu Hongmei[1,2] Wang Tong[1],
Fan Mingde[3], Zhu, Jianxi[1], He Hongping[1]

[1] Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences, Guangzhou 510640, China.
[2] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China.
[3] College of Environment and Resources, Inner Mongolia University, Hohhot 010021, China.

yuanpeng@gig.ac.cn

Porous carbon materials obtained by using the templated method have received a great deal of attention because of their extensive applications in gas separation, water purification, catalytic reaction, and electrochemical processing. In the present work, hierarchically porous carbons with large surface area and high pore volume were prepared by using two types of diatomites as both template and catalyst. Very interesting characteristics of the porous structures of the diatomite-templated carbons were showed. The macroporosity and microporosity of the obtained carbons were derived from the replication of diatom shell and the reconfiguration of the carbon film, respectively. The macroporosity of carbons was strongly dependent on the original morphology of the diatom shell template. One macroporous structure was composed of carbon plates connected by carbon pillars and carbon tubes, which were resulted from the replication of the central and edge pores of the diatom shells with disc-shaped morphology, respectively. The other consisted of carbon tubes replicated from canoe-shaped diatom-shells. The acidity of diatomite dramatically affects the porosity of the carbons, more acid sites of diatomite template resulted in higher surface area and pore volume of the carbon products. The obtained carbons exhibit surprisingly larger adsorption capacity for the large-sized solvent naphtha and small-sized methylene blue than the commercial activated carbon because of the hierarchical porosity. Moreover, the obtained carbons are readily reclaimed and regenerated uses for the adsorption.

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PB16

THE CIVIL ENGINEERING USE OF METHYLENE BLUE DYE ADSORPTION ON FINE MINERAL PARTICLES

Duc M.[1],*, Chen C.W.[1], Maloula A.[1], Hamard E.[2], Descantes Y.[2]

[1]IFSTTAR, Dpt Géotechnique, Eau et Risques, 58 Boulevard Lefebvre, 75732 Paris, France.
[2]IFSTTAR, Dpt Matériaux, Route de Bouaye 44344 Bouguenais, France.

myriam.duc@ifsttar.fr

To prevent pathologies in asphalt pavement (especially the degradation at the claycoated aggregate / bitumen interface in contact with water), the practice in most of European countries requires the use of sandy-aggregates with a low content of fine particles defined as the fraction < 63 µm that contains the < 2 µm fraction associated to clay. France, Belgium and Denmark chose to evaluate the conformity of sandyaggregates products by checking clay content instead of applying a systematic washing of aggregates. The methylene blue dye (MB) adsorption test (EN 933-9 [1]) is used to confirm the harmfulness of the fine fraction [2]. The adsorbed MB amount is related to the specific surface area (and the surface charge) of fine particles and is especially sensitive to the swelling clay presence (as montmorillonite) [3]. So, the quantity of quarry dead that can represent more than 50% of the extracted aggregates in a quarry depends on the protocol of MB measurements and its accuracy. But, in the last decencies, this protocol changed while the limits of conformity did not vary implying a waste in natural resources. The protocol change concerns the drying or not of the material before the MB adsorption measurement. We present here first results comparing adsorption by varying the MB protocol and expose how a better comprehension of the surface charge and surface area behavior of fine particles with variable mineralogy can help to improve the classification of conform and unconfirmed sands. Finally, limits of conformity based on MB value should be revised and discriminated with the clay quantity and mineralogy present in sandyaggregate by comparing MB value with asphalt pavement behavior. A treatment of unconformed aggregates (with lime for example) may be an alternative to lower the waste quarry and save the natural resources.

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PB17

SIMULATION GEOLOGICAL ENVIRONMENTAL SHORTAGE WATER OF GROUNDWATER AND THE POSSIBILITY OF ACTIVITY EARTHQUAKE JAFARAH BASIN NW LIBYA

Elosta Fathi

People's Committee for Education and Scientific Research in Tripoli
Jganzor academy postgraduate studies Earth sciences Department Geological Section

Hmbstf@yahoo.co.uk

Libya is poor countries water that does not have any periods of water surface due to the groundwater nature and it fell within climate semi-arid where of long-range and geological Major role in shaping the nature feature of the region during the era of Oligocene and Pleistocene during the time trio and quartet .it is believed that al-Jafara Basin a time during the quartet was completed for the construction of natural water during Pleistocene and the Jafara basin is water one of the most important sedimentary basins which fed the western region stretching from the five east to come in contact the sea west toward the Tunisian border were heading southwest towards Mslath offer 150 km and length of 130 km and displays

The pelvis to the operations of cracking and sediment to the emergence of a group of fractures to the northwest and south-east until the abu-krch mountain distance of 100 to 200 m about to turn east and west to includes the crack Azizyah the great to the deposits of the valley and mud where they became the basin exposed to the abortions and drilling of wells without considering the natural conditions which may cause environment problem such as earthquake and which is under the ground to it annually to almost one million earthquake does not feel people are mostly either weak or to occur in areas humans or don not feel earthquake usually only when is intensity to 4 degrees on Richter scale and is great when the power up to 7 degree on Richter scale .Jafara Basin of areas may be subject earthquake due to low water levels underground and a set of faults with fracture that may energy operation earthquake slope because of the low pressure the class because of the exploitation of water led to the edges and cracks parallel to the contour lines may relate to these cracks together which increased the breadth a result of increased landing differential layers due to low pressure on the natural equilibrium line and the lowering of fresh water and drained ,the establishment basin faults and fractures as a result of the tensile and compression of the layers ,causing gaps and depressions mainly Azizyah refraction is a great inverted from he spoke seismic basin where rocks may bend and stone energy and when sliding occurs in the areas of weakness and focus earthquake that are at a depth of 20 km and which have a depth of 700 km to occur by the removal of emerging major fault due excessive pressure on the depletion of starch water located between the layers which may occur sudden movement of the energy accumulated and stored on floppy mud millions of years .The cracks are formed far from the spacing of the compression and accompanied by the landslides which may pose and between the spaces between particles of materials and there is a direct relationship between the edges of the panels on the sides of continents and fault so that the primitive edges to slip angle of 540 degree, the Jafara Basin has easy access four water reservoirs which include the formation Al-Azizyah cover the stones and sand with limestone formation Abuchebo covered limestone formation and composition of Kkih and Qasr-al-Haj and the quantity of water in this basin about 4.2x6100 km$^{3.}$

We will try in this paper to speak on the problem of depletion of the water Jafara basin water north-west Libya and seismic indicators which may occur due to the increased pressure drop between pressure class and low water pressure due to water depletion.

PB18

AN INVESTIGATION INTO HEAVY METAL REMOVAL FROM CONTAMINATED SEDIMENTS USING SOIL WASHING

Eswayah A.*

Biotechnology Research Centre, P. O. Box: 30313, Tripoli, Libya

abdurlb@yahoo.com

It is agreed that sediments are vulnerable to contamination by heavy metals (e.g. copper, lead, and Zinc) which can cause significant damage to the environment and human health as a result of their motilities and solubilities, the sources of contamination are often associated with human activities, such as Landfill operation, electrical generator and industrial estates. This study was undertaken to review the efficiency of soil washing in remediating heavy metal- contaminated sediments of a small lake using chemical reagents in batch system. The concentrations of copper, lead, zinc and nickel were measured in sediments collected from the site, the samples were subjected to washing reagents using solutions of ethylenediaminetetraacetic acid (EDTA), hydrochloric acid and citric acid, the contact time, temperature and pH were taken into consideration. All measurements of target elements were carried out by flame atomic absorption spectrometer. The data obtained showed that HCl and citric acid are effective in removing Pb, Zn and Ni, and less effectiveness in removing copper from the sediments. On the other hand, EDTA was effective in removing the metals of interest. Of the washing reagents tested, EDTA solution was generally more effective for removing copper, lead, zinc and nickel from the sediments samples. In addition EDTA can be reused many times.

Keywords: soil washing; heavy metal; washing reagents.

PB19

REMEDIATION OF PAH-CONTAMINATED SOILS BY MAGNETITE CATALYZED FENTON-LIKE OXIDATION

Usman M. [1,2],Faure P.[2]*, Ruby C.[1], Hanna K.[3,4]

[1] LCPME, UMR 7564 CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600, Villers Les Nancy, France
[2] G2R, UMR 7566, CNRS-Université de Lorraine, 54506, Vandoeuvre Les Nancy, France
[3] Ecole Nationale Supérieure de Chimie de Rennes, UMR CNRS 6226 "Sciences Chimiques de Rennes", Avenue du Général Leclerc, 35708 Rennes Cedex 7, France
[4] Université Européenne de Bretagne, France

pierre.faure@g2r.uhp-nancy.fr

This is the premier study reporting the degradation of polycyclic aromatic hydrocarbons (PAHs) through Fenton-like oxidation catalyzed by magnetite. Kinetic degradation of PAHs was studied at circumneutral pH by treatments: (i) H_2O_2 + soluble Fe^{II} (F), (ii) H_2O_2 + magnetite as iron source (FL) and (iii) H_2O_2 alone without catalyst (HP). Results show that oxidation of a model PAH compound (fluorenone) spiked on sand resulted in its complete removal by FL treatment but degradation did not exceed 20% in HP or F systems. However, in two PAHs polluted soils (sampled from coking plant sites), negligible oxidation of 16 PAHs was observed regardless of the catalyst used: soluble Fe^{II} or magnetite. Then organic extract separated from these soils was added to sand and after evaporation of the solvent, oxidation was performed which resulted in more than 90% of PAHs removal by FL as compared to 15% by F or HP systems. These removal extents decreased by a factor of two when the organic extracts were oxidized in the presence of original soil.

PAHs degradation extent was improved in soils pre-treated with availability-enhancement agents such as ethanol or cyclodextrin and also with thermal pre-treatment (60, 100 a,d 150°C) during one week under inert atmosphere.

Degradation was non-selective and no by-products were observed by GC–MS and µFTIR. Treatment efficiency was highly limited by PAHs availability in soils and the soil matrix effect. This study points out the promising efficiency of magnetite for PAHs oxidation at circumneutral pH over soluble Fe^{II} in contaminated soils, and has important implications in the remediation of contaminated soils.

PB20

DEGRADATION OF CARBAMAZEPINE BY TRAMETES VERSICOLOR STRAIN GROWN ON VARIOUS ORGANIC SUPPLEMENTS

Semrany S.[1,2]*, Popa C.[3], Favier L.[1], Djelal H.[4], Taha S.[2], Amrane A.[1]

[1] Ecole Nationale Supérieure de Chimie de Rennes, Université de Rennes 1, CNRS, UMR 6226, UEB, General Leclerc Av., CS 50837, 35708 Rennes Cedex 7, France
[2] Plateforme Azm pour la Recherche en Biotechnologies et ses Applications, LBA3B, EDST, Université Libanaise, Mitein st., Tripoli, Lebanon
[3] Dunarea de Jos University, FSIA, 47 Domneasca st., 800008 Galati, Romania
[4] Ecole des Métiers de l'Environnement, Ker Lann Campus, 35170 Bruz, France

samer.semrany@ensc-rennes.fr

During the last decade, pharmaceutically active compounds (PhACs) have emerged as a major class among water pollutants. In fact, these molecules disrupt the proper physiological processes in living beings, even when present at low concentrations of nanograms per liter of magnitude. Among PhACs, Carbamazepine (Cbz), a widely used antiepileptic drug, is known to be one of the most recalcitrant. Indeed, it persists in water after conventional biological treatment by activated sludge [1]. Recent research showed that filamentous fungi, producing lignolytic enzymes (such as laccases, manganese and lignin peroxidases), can under certain conditions, degrade bio-recalcitrant organic compounds with complex chemical structure.

The purpose of this study was to test the capacity of a filamentous fungus strain, *Trametes versicolor* DSM 11269 to remove Cbz, with or without a carbon co-substrate. Batch experiments were conducted in 500 mL conical flasks containing 250°mL of a mineral medium [2], previously sterilized at 121°C for 20 minutes. Cultures were performed at an initial pH of 7 at 22°C and a stirring speed of 210 rpm. Three co-carbon substrates: glucose, phenol, and tryptophan, were tested at an identical initial concentration of organic carbon (400 ppm C). For each tested co-substrate, cultures were performed in absence or presence of target compound. Cbz was added at an initial concentration of 5 ppm. Samples were taken regularly over 21°days. The measured parameters were: pH, concentrations of Cbz and carbon co-substrates analyzed by HPLC. Enzyme activity was also determined in order to evaluate laccase production.

Results have shown that the metabolic activity of the fungus is reflected by pH decreasing and consumptions of carbon co-substrates. It was also revealed that among the three tested organic growth supplements, glucose leads to the highest biomass concentrations and enzyme activities, in presence or in absence of Cbz. It was observed that the presence of Cbz in the culture medium does not inhibit *Trametes versicolor* growth in the presence of an easily assimilated carbon co-substrate. This is in accordance with other published results [3]. In presence of phenol and tryptophan, low concentration in biomass and low enzyme activity were noted. In terms of Carbamazepine elimination, a degradation of about 20% was observed in the presence of glucose and in the medium without co-substrate. These results are very promising given the bio-recalcitrance of this compound. Work is in progress to improve fungal culture conditions to enhance the reduction yield of the target molecule.

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PB21

SYNERGISTIC EFFECTS IN MIXED COLLECTOR SYSTEMS: HF-FREE FLOTATION METHOD FOR SEPARATION OF FELDSPARS ORE

Filippov L.O.[1]*, Filippova I.V. [1], Ancia A.[2]

[1]Université de Lorraine, LEM UMR 7569 CNRS, BP 40, 54501 Vandoeuvre-lès-Nancy Cedex, France
[2]Imerys Ceramic Centre, 8 rue Soyouz 87068 Limoges, France.

lev.filippov@univ-lorraine.fr

Conventionally, feldspar is separated from quartz using an amine-type surfactant as cationic collector in acidic circuit. Hydrofluoric acid (HF) is traditionally used in plant practice during the conditioning step as a pH regulator and an activating agent providing an excellent selectivity of quartz/feldspar separation. The HF reacts with aluminol sites or silanol sites on the feldspars surface forming alumino-silicon fluoride complexes. The amine molecules are then preferentially adsorbed on these negatives sites allowing the formation of an amine monolayer on the feldspar surface. In other hand, fluoride ions can generate silica depression by exchanging silicon surface hydroxyl groups with fluoride ions. It results a reduction in the number of negative surface silicon sites and a decrease of the amine adsorption on the quartz. Thus a significant difference in surface hydrophobicity for two minerals is obtained providing an excellent selectivity of flotation process at pH below 2.5. However, a corrosive chemical environment and the ecological impacts from the potential fluoride ion contamination are limiting factors for the use at industrial scale. This paper presents the investigations for the use of non linear long-chain isoalcools in the mixed cationic/non-ionic system to develop a new HF-free environment friendly flotation method for feldspar/quartz separation.

Investigations of the amine-feldspar interactions in the absence and presence of non-linear long-chain alcohols were carried out using infrared spectroscopy in diffuse reflectance mode. A co-adsorption of both long-chain alcohols and amine cations was deduced from the 4-8 cm-1 shifting of C-H bending. The presence of alcohol molecules led to formation of a closed packed layer only on the surface of feldspars due to specific adsorption on aluminol sites. The highest order and packing at the feldspar surface were observed with a particular alkyl chain structure as Guerbert alcohols.

A new flotation process was developed and tested at both lab and pilot scales on different feldspar ores. This method is able to provide a satisfactory feldspar recovery, with high selectivity when used in particular conditions. New HF-free process is strongly dependent on the pH range and sulphuric acid consumption during conditioning steps, as well as the ratio of main collector and non-ionic additive.

PB22

REDUCING OF CO_2 EMISSION BY CARBONATION OF SALINE WASTE SOLUTION

Filippov L. O.*, Filippova I., Piriou P., Grandjean M.

LEM, UMR 7569 CNRS, Nancy-University, ENSG, BP 40, 54501 Vandoeuvre-lès-Nancy Cedex, France

lev.filippov@univ-lorraine.fr

Accelerated carbonation begins to be used for the treatment of wastes and contaminated soils and for the sequestration of CO_2. This kind of mineral sequestration of CO_2 is adapted to modern carbon management, which main ideas are the capture and sequestration of CO_2, the increase of efficiency of energy conversion and the use of low carbon or carbon free energy sources. Thus, carbonation of the residues of the ammonia-soda process, which makes them passive and avoids further phase transformation, is a modern and promising way of dealing with such hazardous for environment materials, mainly through chloride leaching.

This work deals with the carbonation of residual brines produced during the manufacture of soda ash to avoid the unsuitable phase transformation during the land storage. The study resulted in a demonstration pilot, which showed the feasibility of such an approach and the possibility of his extension to an industrial scale.

The phases presents in the residual brines sensitive to carbonation are identified and an magnitude order of carbonation of them is obtained by coupling infrared spectroscopy and X-ray diffraction methods, Raman spectroscopy and transmission electron microscopy. Thus, the first phase which disappears is CaOHCl, followed by the disappearance of $Ca(OH)_2$ at pH around 10, then calcium silicate hydrate (C-S-H) disappear for pH around 8.5 and finally $Mg(OH)_2$ at pH around 7.5.

It must be noted that carbonation is not only interesting because of the precipitation of new mineral phases (calcium carbonate essentially) from different mineral. Indeed it also deeply modifies the global equilibrium of the system, leading to the decrease of mobility of elements such as aluminium, which is responsible of the appearance of unsuitable phases during land-storage.

Due to very high reactivity of the precipitated minerals, new carbonate phases are studied for the neutralization of combustion gases containing SO_2. Very fine carbonate particles are first precipitated in brines by CO_2 bubbling in a carbonation column. Then calcium carbonates react with SO_2 to produce calcium sulfates. To understand the behavior of carbonates during desulphurisation, a chemical reaction model was considered to optimize the experimental parameters. Results were discussed taking into account the hypothesis that the reactivity is related to carbonate surface hydration.

Another way of valorisation of this material was studied and proposed to manage the time of curing and the mechanical properties of cement concrete used in the aggressive environment such as acid solutions or see water.

Carbonation of the residual brines allows to obtain a neutral pH which considerably reduce the land storage impact on environment and shorten by around 10 % the global CO_2 emission of the ammonia-soda process.

THE REMOVAL CHARACTERISTICS OF NITRATE AND PHOSPHATE BY MG-AL-LDHS

Halajnia A.[1], Oustan S.[2], Najafi N.[3], Khataee A.R. [4], Lakzian A.[5]

[1] PhD. Student of Soil Science, University of Tabriz, Iran, [2] Associate Professor of Soil Science, University of Tabriz, Iran, [3] Assistant Professor of Soil Science, University of Tabriz, Iran, [4] Associate Professor of Applied Chemistry, University of Tabriz, Iran, [5] Associate Professor of Soil Science, Ferdowsi University of Mashhad, Iran

halajnia@yahoo.com

Nitrate easily moves through the soil profile and eventually enters the groundwater as a common contaminant. Recently the possibility of using layered double hydroxides (LDHs) to improve nitrate retention capacity (NRC) of soils has been proposed [2]. For successful application of LDHs to remove nitrate, these compounds should have high selectivity for nitrate adsorption in the presence of other anions, particularly phosphate, in complex solutions such as soil solution. In the present study Mg-Al LDHs with M^{2+}/M^{3+} ratios of 3:1 and 4:1 were synthesized by the coprecipitation method [1]. The synthesized LDHs were characterized by XRD, TGA and SEM techniques. The LDHs were compared in terms of ion adsorption isotherm and selectively in the presence of common anions in the soil solution. Results showed that the M^{2+}/M^{3+} ratio had a significant effect on structural and adsorption characteristics of Mg-Al-LDHs. The anion exchange capacity of Mg-Al-LDH (3:1) and Mg-Al-LDH (4:1) were determined as 192.7 and 160.6 cmol kg^{-1}, respectively. Nevertheless, Mg-Al-LDH (4:1) showed higher BET specific surface area (64.42 $m2g^{-1}$) compared to Mg-Al-LDH (3:1) (21.03 m^2g^{-1}). The percentage of phosphate adsorbed from the solution contains 1 mM nitrate, phosphate, sulfate and bicarbonate decreased with decreasing M^{2+}/M^{3+} ratio. However, the reverse was true for nitrate (Fig1, left). The experimental data for phosphate adsorption by Mg-Al-LDH (3:1) and Mg-Al-LDH (4:1) fitted well into Freundlich and Langmuir isotherms, respectively. For nitrate a good agreement between the experimental data and Langmuir isotherm was observed. The highest adsorption capacity from Langmuir isotherm was obtained for Mg- Al-LDH (4:1) probably due to the nitrate ion-sieve property of these LDH. The Mg-Al- LDH (3:1) showed a higher distribution coefficient for phosphate compared to nitrare in all equilibrium concentrations. However, the Mg-Al-LDH (4:1) showed a higher distribution coefficient for phosphate at lower equilibrium concentrations and for nitrate at higher equilibrium concentrations (Fig 1, right).

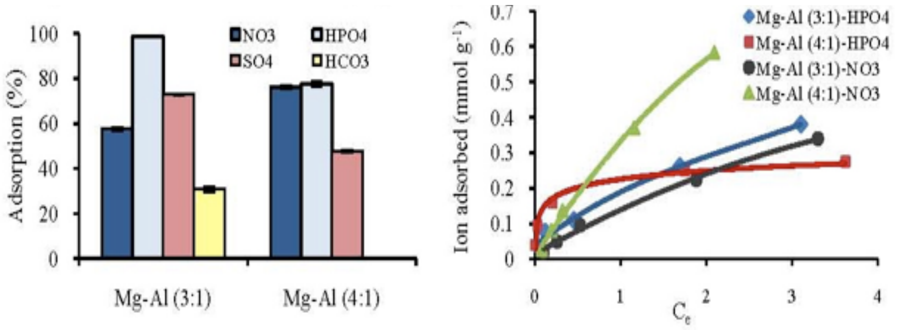

Fig 1: Percentages of nitrate and phosphate adsorbed by the LDHs (left). Nitrate and phosphate adsorption as a function of equilibrium concentration (right)

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PB24

ACTIVATED SLUDGE BEHAVIOR IN THE PRESENCE OF HOUSEHOLD MICROPOLLUTANTS

Pasquini L.[1], Hassenboehler L.*[2], Colla G.[1], Merlin C.[3], Munoz J.F.[4], Pons M.N.[5], Görner T.[1]

[1] LEM - CNRS, Université de Lorraine, 15 Avenue du Charmois, 54501 Vandœuvre-lès-Nancy cedex, France
[2] GEMCEA, 149 rue Gabriel Péri, 54500 Vandœuvre-lès-Nancy, France
[3] LCPME, CNRS, Université de Lorraine, 15 avenue du Charmois, 54500 Vandœuvre-lès-Nancy, France
[4] Laboratoire d'Hydrologie de Nancy, ANSES, 40 rue Lionnois 54000 Nancy, France
[5] Laboratoire Réactions et Génie des Procédés - CNRS, Université de Lorraine, 1 rue Grandville, 54001 Nancy cedex,

lucille.hassenboehler.1@etumail.uhp-nancy.fr

Our everyday life is a source of pollution through domestic wastewater. Many of increasingly used pharmaceuticals products or complex chemicals, which offer household facilities (detergents, corporal care, food additives, anti adhesive treatments…), are already thought to be a possible threat to environmental health and safety. It appears necessary to assess the impact of these micropollutants on activated sludge and to assess their concentration in wastewater treatment systems in order to derive safe conclusions about their fate and their possible threat level.

The aim of this study was to evaluate the impact of eight molecules: erythromycin, ofloxacin, ibuprofen, triclosan, 4-nonylphenol, sucralose, perfluorooctane acid (PFOA), and perfluorooctane sulfonate (PFOS). First the growth-based toxicity tests were performed with *Escherichia coli MG1655*. Then the impact of above mentioned molecules on municipal activated sludge was studied in batch reactors, where each micropollutant was added to 3 L of mixed liquor (wastewater and sludge) at three levels of concentration. Different parameters were followed during 24h:

- The biomass capacity to degrade or adsorb micropollutants was performed using a solid phase extraction method followed by liquid chromatography tandem mass spectroscopy analysis of the liquid (water) and solid (sludge) phases.
- The production of extracellular polymeric substances (EPS) as indicator of bacteria sensitivity to toxic stress was estimated by high-pressure size-exclusion liquid chromatography.
- The biomass capacity to degrade organic matter COD (chemical oxygen demand) and the ammonium concentration were measured by spectro-photocolorimetric methods.

It was found that some molecules (ibuprofen, erythromycin, ofloxacin, 4-nonylphenol and triclosan) were removed from wastewater from 60 % to more than 90 % and for all studied concentration levels while sucralose, PFOA and PFOS were not at all removed from wastewater. Some molecules (erythromycin, ofloxacin, triclosan, 4-nonylphenol) induced an increase of bound EPS in flocs, this was attributed to a protection mechanism of the bacteria.

PB25

FUNCTIONALIZATION OF ORGANIC MEMBRANES BY POLYELECTROLYTE MULTILAYER ASSEMBLIES. APPLICATION TO THE DECONTAMINATION OF AQUEOUS SOLUTIONS CONTAINING METAL TOXIC IONS.

Magnenet C.*, Lakard S., Buron C.C., Lakard B.

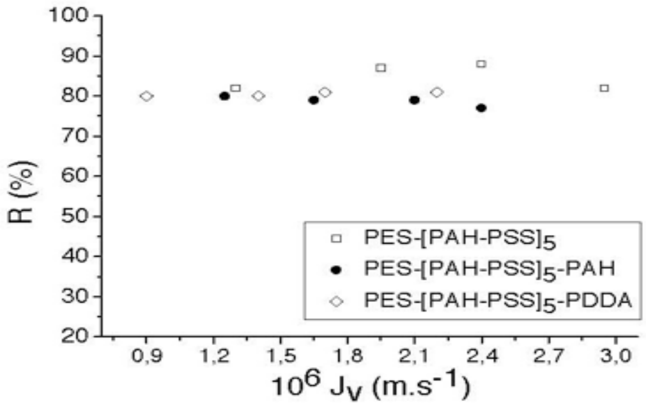
Université de Franche-Comté, Institut UTINAM-UMR CNRS 6213, 16 Route de Gray,
25030 Besançon cedex, France

claire.magnenet@univ-fcomte.fr

After Decher demonstrated the feasibility of the deposition of polyelectrolyte multilayer films (PEMs) by consecutively alternating electrostatic layer-by-layer adsorption of charged polyelectrolytes [1], the LbL technique became a more and more employed method thanks to its simplicity, versatility and efficiency.

The preparation of new membranes with good separation capability is still a major research goal in membrane science. A promising way to combine good separation and high flux is based on the use of composite membranes consisting of a porous support and an ultrathin separation film. The functionalization of an organic polyethersulfone membrane (PES) was performed by alternating deposition of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) (PSS), leading to the formation of a polyelectrolyte multilayer film (PEM). The resulting assembly was characterized by tangential streaming potential measurements to determine the charge of the modified membranes and by Infra-Red spectroscopy [2,3]. Then, the modified membranes were used to perform the ultrafiltration of aqueous solutions containing Cu^{2+} ions. Different operating conditions were tested including : polyelectrolyte concentration, polyelectrolyte nature, thickness of the PEM film or pH of the copper solutions.

These filtration experiments demonstrated that it was possible to obtain a satisfactory retention of the copper ions (88%), thus proving that this type of assembly can be useful for the removal of copper ions from contaminated aqueous solutions.



Copper retention rate (pH=2) as a function of the permeate flux for different PEM-modified membranes.

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PB26

COLLOIDAL-CHEMICAL ASPECTS OF IN-SITU LEACHING OF URANIUM

Mamytbekov G.*, Kozhakhmetov S.

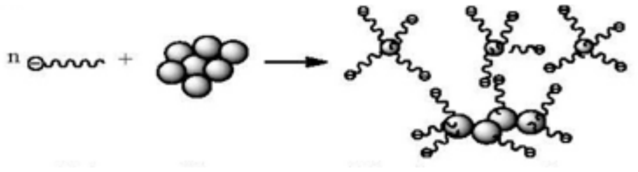
Institute of High Technologies, Almaty, Kazakhstan

mamytbekov@mail.ru

For successful carrying out in-situ leaching (ISL) of uranium it is necessary to define a structure and phase condition and character of permeability of the ore-bearing strata. The last in turn define the mechanism of penetration of the lixiviant in the strata, mechanism of metal leaching and creations of oxidation-reduction geochemical barriers. The simple way of the formation of an underground stream is provided due to the pressure difference between pumping and pumping-out wells because of the loosening and washing out of the ore-bearing particles by special chemical reagents. The difference of the strata pressure increases with the distance between wells and decreases with increasing of permeability of an ore body and dissolving ability of the lixiviant. The factors defining the leaching time of uranium are: a) the distance between wells; b) permeability of an ore-bearing layer; c) the dissolving ability of the leaching reagents.

Because of carbonate strata the process of leaching of uranium in a such condition accompanied by gypsum formation due to interaction of sulphuric acid both with limy and dolomitic breeds. Hence it is necessary to create the conditions at which there would be dissolution of gypsum crusts on the surface ore-bearing particles. It can be reached by increasing of loosening degree of the firm deposits due to the infusion in their structure of a dispersing agents which give to them aggregative stability, but are not capable to dissolve completely. The transfer of deposit in a suspension can be reached by surfactant molecules. The stabilization factor of similar deposits is defined by a charge of the surfactants (negatively charged sulfonol (S) was used). Thus hydrophobic tail of the surfactant molecules is adsorbed on the surface of electroneutral particles of gypsum and polar groups of already adsorbed molecules of surfactant causing the hydrophilizations of the surfaces and forms a double electric layer that provides additional penetration of the leaching fluid and causes effect disjoining pressure.

Scheme of loosening of the firm particles



For fuller dissolution of the gypsum deposits and move of the stream of lixiviant a sulfaminic acid (SAA) was used. The SAA is capable to easily interact with the charged particles and ions and to protect them from loss of aggregate stability due to the electrostatic factor of stabilization. The SAA can similarly stabilize hydroxides, sulfates and uranyl carbonates in its various forms and oxidation degrees. For example

$$Me(OH)_3 + 3\overset{\oplus}{N}H_3\overset{\ominus}{SO_3} \longrightarrow Me(SO_3\overset{\oplus}{N}H_3)_3 + 3H_2O$$

where Me – Fe^{+n}, Al^{+3}

Additionally the cavitational treatment of the leaching liquid promotes its activation, changes its physical and chemical properties, intensifies the leaching processes. For strengthening of cavitational action on the lixiviant the complex of multiple-factor influence on the processed leaching liquid is necessary.

PB27

REDUCING POWER AND CARBON FOOTPRINT OF THE BOUMERDES WASTEWATER TREATMENT PLANT

Souahi F.[1], Mefti A.[1]*, Benbessi A.[1], Sebti K.[1], Igoud S.[2]

[1]Ecole Nationale Polytechnique, 10 avenue Pasteur, B.P. 182, El Harrach, Alger (Algérie)
[2]Unité de Développement des Equipements Solaires, Bou Ismail, Tipaza (Algérie)

meftiafia@yahoofr

Our study is concerned by the Boumerdès wastewater treatment plant with a goal of reducing energy consumption and carbon emissions throughout the chain of treatment and also at the level of the administration and laboratory buildings and outdoor lighting.
Part of the work is also to determine the carbon footprint generated by the station.
Inventory of electric equipment and calculations were done to evaluate energy consumption and cost.
Solutions using renewable energy are proposed in order to cover part of the needs of the wastewater treatment plant and to protect the environment. It consists mainly in the mud treatment to produce biogas by digestion. On a second hand, it is possible to use solar energy to replace electric power especially for lighting.

PB28

SYNTHESIS OF TASK SPECIFIC IONIC LIQUIDS FOR THE METAL EXTRACTION

Messadi Mohamadou A.*, Boudesocque S., Dupont L.

Institut de Chimie Moléculaire de Reims UMR CNRS 7312, Groupe de Chimie de Coordination,
Université de Reims Champagne-Ardenne, UFR SEN, BP 1039 - 51687 REIMS Cedex 2

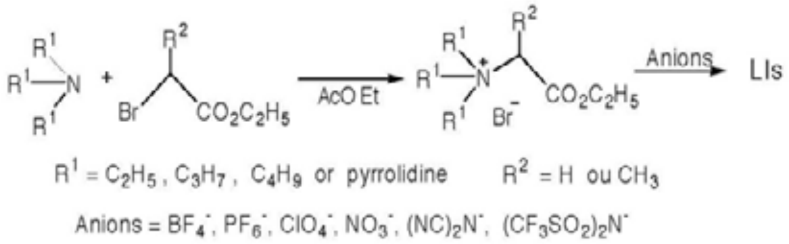
aminou.mohamadou@univ-reims.fr

Ionic liquids are solvent constituted by ions, most often by an association between asymmetric organic cation and an anion, which have a melting point below 100 °C. The discovery of water immiscible ionic liquids naturally suggested their use for biphasic metal extraction in order to replace more toxic organic solvents [1-3].

Our work aims to design cationic organic chelating synthons derived from vegetal or animal renewable resources (betaine, glycine or alanine), which can generate original task specific ionic liquids by association with an inorganic anion. These ionic liquids (ILs) are used in order to develop process for pollution remediation.

The application proposed, in this work, concern the use of ionic liquids for the recovery of heavy metals from industrial effluents by liquid-liquid extraction. One of the sought properties will be to obtain water immiscible IL, liquid at room temperature.

The cationic synthons, obtained in the form of bromide salts (Scheme 1), can generate ionic liquids by metathesis reactions in the presence of the desired anionic salt [BF_4^-, PF_6^-, NO_3^-, $(NC)_2N^-$ (Dca), ClO_4^- and $(CF_3SO_2)2N^-$ (NTf2)].



Scheme 1: Synthetic route of the ionic liquids (LIs)

A series of ionic liquids (ILs) are isolated and characterized by various physicochemical methods (elemental analysis, ^1H and ^{13}C NMR, IR, DSC, viscosity, Karl Fischer titration, crystal XRD).

The extraction of the different metal cations (Cu^{2+}, Ni^{2+} and Pb^{2+}) in aqueous solution by ionic liquids synthesized was performed. The extraction yields, determined by the measurements of the residual metal concentration in aqueous solution, depend not only the length of the alkyl chain of the ammonium but also on the nature of the associated anion. The most promising results are obtained with ILs whose anion has a chelating ability. The mechanism of metal transfer has been studied and was related to the hydrophobicity of the cationic synthon. Increasing the hydrophobicity of the cationic synthon leads to an increase of extraction yield, thus limiting the ion exchange (either an ion of opposite charge from the aqueous phase or an ion of the same charge from the ionic liquid moving into the aqueous phase) and promoting ion pairing extraction [4, 5]. The plating will be considered for metal recovery of the ionic liquid phase.

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PB29

RELATION BETWEEN HYDROUS STRAIN AND THE CATIONIC EXCHANGE PROCESS IN THE CASE OF NA-RICH MONTMORILLONITE : QUANTITATIVE XRD DESCRIPTION

Oueslati W.[1,2]*, Ammar M.[1], Ben Rhaiem H.[1] and Ben Haj Amara A.[1]

[1] UR05/13-01 : Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia
[2]Faculté des sciences de Gafsa, Département de physique, campus universitaire Sidi-Ahmed Zarrouk 2112 Gafsa,

walidoueslati@ymail.com

This work aims at examining, by quantitative XRD analysis, the effect of an applied hydrous strain in the cationic exchange process of a dioctahedral smectite. The hydrous constraint was created by a continuous, in situ, hydration-dehydration cycles using variation of %RH rate. Respectively, The starting, the intermediate and the final stressed samples was deposed in contact with saturated Cd(II), Co(II), Zn(II) and Ni(II) chloride solutions respectively in order to examine the effect of the retained materials stress on the CEC (i.e. Cationic Exchange Capacity) of the host materials. An XRD profile modelling approach is adopted to describe all structural changes created by the environmental evolution of the %RH rate. This investigation allowed us to determine several structural parameters related to the nature, abundance, size, position and organization of exchangeable cation and water molecule in the interlamellar space along the c* axis.

Qualitative results show a considerable change in the hydration behaviour, versus the number of hydration –dehydration cycle, from homogeneous “2W” to heterogeneous “1W- 2W” hydration state indicating an interstratified hydration phase and due probably to a new organization of the interlamellar space content. Quantitatively, the theoretical Mixed Layer Structure suggests the coexistence of more one “crystallite” specie which are saturated by more than one exchangeable cations indicating a partial saturation of all exchangeable sites. Using optimum structural parameter values, deduced from XRD modelling profile approach, some equations which described the evolution of exchangeable cation amount versus the applied hydrous strain were derived.

PB30

DEGRADATION OF INDIGO CARMINE SOLUTIONS BY THIN FILMS OF BIRNESSITE ELECTRODEPOSITED.

Zaied M.[1,2],Peulon S.[1]*, Bellakhal N.[2], Chaussé A.[1]

[1] CNRS - Université d'Evry - CEA, Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, UMR 8587, Boulevard François Mitterrand, 91025 Evry, France

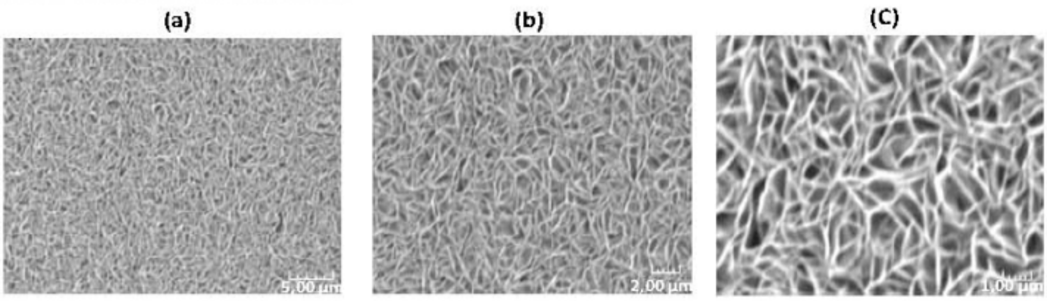
[2] Laboratoire de Chimie Analytique et d'Electrochimie, Faculté des Sciences, Campus universitaire El Manar, 2092 Tunis, Tunisie

sophie.peulon@univ-evry.fr

Many industries generate a considerable amount of colored wastewater causing damage to the ecological system because most dyes are stable to light and are not biodegradable. In order to remove dyes, different methods were developed with success, but generally with high costs or high energetic needs.

In this context, we have shown recently the successful possibility to use thin layers of birnessite (Mn_7O_{13}, $5H_2O$) electrodeposited onto SnO_2, a cheap transparent semiconductor, for discoloring solutions containing dyes like methylene blue as a very interesting solution for environmental applications [1].

These very good results encouraged us further to investigate the possibility to use these thin films for the degradation of another dye: Indigo Carmine (IC). This anionic dye belongs to a highly toxic class of dyes (indigoïd). The spontaneous reactivity of birnessite thin layers was very effective for the degradation and mineralization of this dye, with a possibility to reuse these samples, without energy supply [2]. The birnessite thin film electrodeposited is a very interesting material for the development of a simple and ecologically method applied to the treatment of waste water loaded with dyes.



SEM pictures of birnessite thin films electrodeposited onto SnO_2.

(a) X 1000, (b) X 5000, (c) X 10000.

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PB31

CHARACTERIZATION OF LOW DISPERSITY ANIONIC MULTI-RESPONSIVE CORE-SHELL POLYMER PARTICLES

Pinheiro J. P.[1],* Moura Leila[2], Fokkink Remco[3], Farinha J. P. S.[2]

[1]IBB/CBME, Departamento de Química e Farmacia/ Faculdade de Ciências e Tecnologia Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal.
[2]Centro de Química-Física Molecular and IN - Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, 1049-001 Lisboa, Portugal.
[3]Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen, The Netherlands.

jpinhei@ualg.pt

We prepared anionic multi-stimuli responsive core-shell polymer nanoparticles with very low size dispersity. By using either acrylic acid (AA) or methacrylic acid (MA) as a comonomer in the poly(N-isopropyl acrylamide) (PNIPAM) shell, we are able to change the distribution of negative charges in the nanoparticle shell [1].

The particles have a glassy poly(methyl methacrylate) (PMMA) core of ca. 40 nm radius and a cross-linked PNIPAM anionic shell with either AA or MA comonomers. The particles, p(N-AA) and p(MA-N) respectively, have the same total charge but different charge distributions. While the p(MA-N) particles have the negative charges preferentially distributed towards the inner shell, in the case of the p(N-AA) particles the charge extends more to the particle outer shell.

The volume phase transition temperature (TVPT) of the particles is affected by the charge distribution and can be fine-tuned by controlling the electrostatic repulsion on the particle shell (using pH and ionic strength). By suppressing the particle charge we can also induce temperature-driven particle aggregation.

The particle size, volume phase transition temperature and aggregation state can be modulated using temperature, pH or ionic strength, providing a very versatile platform for applications in sensors, medical diagnostics and environmental remediation.

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PB32

EFFECT OF CHLORIDE SALTS ON THE MEAN BUBBLE DIAMETER IN A FLOTATION COLUMN

Piriou P.,* Filippov L.O.

Laboratoire Environnement Minéralurgie, Université Lorraine, UMR 7569, Vandoeuvre-Lès-Nancy, France

patrice.piriou@univ-lorraine.fr

Flotation using sea water or industrial residual brines is a great upcoming challenge for mineral processing. Changes of physico-chemical conditions induced by the use of such liquid phases should be investigated. This study tries to understand the role of cations of chloride salts on flotation characteristics such as the mean bubble diameter and the bubble diameter distribution.

Solutions of chloride salts (NaCl, $MgCl_2$ and $CaCl_2$) dissolved in fresh running water are used as feeding of a three-meter high flotation column. The column operates in closed circuit with different liquid rates and different gas rates. The range of superficial liquid rate, JL, goes from 0.19 to 1.70 $cm.s^{-1}$. The range of superficial gas rates, JG, goes from 0.19 to 1.69 $cm.s^{-1}$. Gas hold-up is measured in the collection zone of the flotation column thanks to the pressure method. Drift flux analysis is used to obtain the mean bubble diameter between the two pressure points Dobby et al. [1].

Experiments show that presence of dissolved NaCl in the water effectively inhibits bubble coalescence, Craig et al. [2], allowing to obtain fine bubbles with a low bubble diameter dispersion. On the other hand, presence of dissolved $CaCl_2$ in the water results in a large dispersion of bubble diameter, with a slightly higher mean bubble diameter. Mg^{2+} seems to have a behaviour halfway between Na^+ and Ca^{2+}, when using lower concentrations. When monovalent cations (Na^+) are added to a solution of bivalent cations (Ca^{2+}), mean bubble diameter increases for low gas rates and decreases for high gas rates.

Thus, cations of the chloride salts clearly have not the same impact on the inhibition of bubble coalescence and on the bubble diameter distribution. The characterization of the liquid phase used for flotation separation should not only focus on the concentrations of salts, that to say the ionic strength, but also on the specificion effect of its cations.

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PB33

EFFECT OF CATION COMPETITION ON STRONTIUM UPTAKE BY TYPE 4A ZEOLITE FROM MULTI-COMPONENT AQUEOUS SOLUTIONS

Prelot B.*, Araïssi M., Ayed I., Marchandeau F., Zajac J.

Institut Charles Gerhardt de Montpellier, CNRS UMR 5253, Université Montpellier 2
Equipe Agrégats, Interfaces et Matériaux pour l'Energie, C. C. 1502,
Place Eugène Bataillon, 34095 Montpellier cedex 5, France;

prelot@um2.fr

Heavy metals and radionuclides are highly toxic environmental pollutants and, as such, should be completely removed from aqueous streams. Efficiency of remediation technologies based on sorption phenomena at the solid-liquid interface has been proven and a variety of sorbents have been tested in such applications. Motivated by overall cost reduction, the use of low-cost natural materials or waste products from certain industries frequently leads to serious difficulties in controlling the treatment process because of a considerable heterogeneity of the solid surface. There arises question as to whether inorganic materials, possessing regular porosity and good radiation and thermal stability, can be also efficient in removal of heavy metals and radionuclides from aqueous streams under conditions of competition among various ionic species.

The intention of the present work was to study the strontium-selectivity of a commercial 4A zeolite (Somez, France) in multi-component aqueous phase. Liquid chromatography was exploited to measure the individual and composite sorption isotherms of Sr^{2+} from nitrate aqueous solutions containing other ionic species (e.g., Cs^{+}, Ca^{2+}, Ba^{2+}, Cd^{2+} and Mn^{2+}). The composition of the mobile phase was carefully optimised to avoid the peak overlapping effects when analysing multi-component supernatants. Speciation of the $Me/OH^{-}/NO_3^{-}$ systems was simulated with the aid of JCHESS® software to account for the metal hydrolysis in the aqueous phase. Isothermal titration calorimetry was the basis of the systematic study of interactions involved in the sorption phenomena. Different exothermic and endothermic regimes were observed on the plot of the enthalpy of displacement vs. amount adsorbed, indicating the changes in the various enthalpy contributions related to adsorption, desorption, dehydration and rehydration steps. This behaviour illustrates well the complexity of the overall displacement process.

PB34

VARIATION IN INORGANIC AND ORGANIC SOIL SOLUTION COMPOSITION INDUCED BY INCUBATION OF AN ACID SOIL WITH ORGANIC WASTES

Rodríguez-Liébana J.A.[1], Fernández Espinosa A.J.[2]*, Peña A.[1], Mingorance M.D.[1]

[1]Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), 18100-Armilla, Granada (Spain).
[2]Departamento de Química Analítica, Universidad de Sevilla, 41012 Sevilla (Spain)
[3]Instituto de Recursos Naturales y Agrobiología (CSIC), 41012 Sevilla (Spain)
[4]Departamento de Biología Vegetal y Ecología, Universidad de Sevilla, 41080 Sevilla (Spain)

anjose@us.es

During the incubation process of soil + organic wastes changes in soil solution composition occur, with possible implications on retention or availability of nutrients or other compounds. Among them, low molecular weight organic acids (LMWOA) are recognized to be of major importance in a number of soil and plant processes, being the ones most commonly identified oxalate, citrate, acetate and formate [1]. In addition, inorganic composition of soil solution may also evolve with waste addition. Therefore, we evaluated the changes in soil solution composition of a mine soil added with organic wastes.

The soil, collected in a mine tailing (Nerva district, SW Spain) is coarse-textured, extremely acid (pH 2.4), has low organic carbon content (1.4%), low cation exhange capacity and unbalanced essential nutrient content. Soil was limed to rise pH to physiological values, and then added (5 and 10% w:w) with organic wastes: sewage sludge composted with pruned olive wastes (CLV) and air-dried stabilized sewage sludge (SSL). The soil was incubated at 40% field capacity for 2 months. Soluble ions were extracted by shaking soil, for 1 min, with ultrapure water (1:10 ratio), then centrifuged, filtered and analysed by ion chromatography. Organic and inorganic ions ($HCOO^{-,}$ CH_3COO^-, $C_2O_4^{2-}$, $C_8H_4O_4^{2-}$, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}) were periodically determined during the incubation process.

Native soil solution composition was dominated by SO_4^{2-}, NO_3^-, Ca^{2+}, K^+, Mg^{2+} and NH_4^+. With increasing pH, SO_4^{2-} concentration was strongly increased (up to 3- fold). An impact of amendment application on soil solution composition could be identified for NO_3^-, K^+, Cl^- and NH_4^+. Addition of CLV, but not of SSL, caused an increase in NO_3^- (> 20-fold), while the addition of SSL but not of CLV enhanced NH_4^+ (> 300-fold). Concentrations of Cl^- and K^+ increased with both amendments, more for SSL than for CLV. In general, the amount of LMWOAs tended to increase with the dose of organic waste, with higher levels of formate and acetate than oxalate and phthalate. Incubation time did not affect the LMWOA content in soil solution. Organic acids, which due to their lability could be utilized by most soil microorganisms, represent only between 0.1 and 1.1% of the total soil solution.

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PB35

WATER PURIFICATION FROM SURFACTANTS BY NATURAL ADSORBENTS

Sineva Alisa V.

Lomonosov Moscow State University, Faculty of Chemistry, Moscow, Russia

asineva@mail.ru

Today, the world faces an urgent task to protect and manage water resources. The role of surfactants as a factor of surface- and ground-water pollution is comparable to that of oil pollution in world oceans. Therefore, the most acute problem is the quality of fresh water [1].

The method of purification of wastewater from different types of surfactants selected was the adsorption at the surfactant solution–air and surfactant solution adsorbent interfaces. This method is the basis of adsorption technologies for the extraction of surfactants from aqueous solutions and wastewater treatment.

In this study, the adsorption of synthetic surfactants from aqueous solutions, namely, sodium dodecylsulfate, cetyltrimethylammonium bromide (_TAB), and Triton X-100 was investigated. The adsorbents used were natural microheterogeneous materials with a potential for use in water treatment systems. In particular, nonactivated shungite of the third type, mechanically activated charcoal, mechanically activated shungite of the first and third types, and mechanochemically activated shungite of the third type were tested, and, for every surfactant, the most effective adsorbents were chosen.

Since the desorption of surfactant may be a problem for purification of water from CTAB when shungite of the third type is used we also discuss the formation of hydrocarbon aggregates chemically bonded to mineral surface oxides. Traditional adsorption isotherms combined with thermodynamic analysis of the standard Gibbs energy changes of adsorption and accompanying micellization of surfactants in water can be applied to describe the regularities of water treatment and the rational selection of adsorbents based on the interface phenomena.

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PB36

MOBILE INFRASTRUCTURE IN A AGRICULTURAL PRODUCTION

Traballi Rogerio*, Traballi Amanda G. M., Roberto Ramos Carlos, Leme Ednilse, Duarte Leandro Uliana, Hellmeister Pedrosa Ylara

Universidade Paulista - UNIP

rogeriotraballi@me.com

Key Words: Agricultural, production, Brazil, Mobile

Agricultural production when you see its system of storage, distribution and logistic as a whole but the final price represent much of infrastructure,distribution and logistic in Brasil.

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PB37

BEST NUMBER OF SAMPLE: SOIL FERTILIZED WITH SEWAGE SLUDGE

Traballi R.C.[1]*, Guerrini I. A.[2], Corrêa J.[3], Breda C.C.[4], Pedrosa Ylara H.[1]

[1]Universidade Paulista -UNIP
[2]UNESP
[3]EMBRAPA
[4] UFMT

rogerio@traballi.com

The goal of this paper was to apply statistical techniques in determining the minimum number of soil samples to be collected in a fertilized area with sewage sludge which, after analyses, represent, with high confidence, the chemical composition of the analyzed soil. To this end parcels of 486 m^2 were used, consisting of 9 lines set out in a 3 meter interval and in each line 9 *Mata Atlântica* plants, alternating with a mix of pioneering, secondary and climax plants were planted at a 2 meter interval, totaling 81 plants. These plants were fertilized with sewage sludge in the following doses: 2,5; 5,0; 10,0; 15,0 and 20,0 t ha^{-1}. For every dose of sewage sludge, 5, 10, 15, 20, and 25 simple soil samples were collected, thus composing the samples that were sent out for laboratory analysis. The experimental design followed the random block method with four repetitions, in an outline of subdivided parcels, where the parcels were made of doses of sewage sludge and the sub parcels of number of samples collected. The measured values of Ca, Mg, P and K obtained from the analyzed soil were varying, confirming to the doses of sewage sludge applied, but the number of samples were not influenced by agricultural practice, leaving the spatial variability for each type of variable. Based upon obtained results it can be concluded that, in order to determine pH, $H^+ + Al^{+3}$ and M.O. of the variables, after applying 20 t ha^{-1}, it is necessary to collect, at least, 5 simple samples as a base for a reliable composed sample. To determine the values of K, Ca and Mg, with high confidence, 20 or more simple samples were needed to make such a composed sample.

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PB38

EFFECT OF THE FRACTAL MICROSTRUCTURE OF CLAY ON THE SEQUESTRATION OF A POLLUTANT IN SOILS

Woignier T.[a]*, Soler A.[b] , Clostre F. [c], Fernandes P.[c] ,Macarie H.[a] ,Jannoyer M.[c]

[a]UMR CNRS 7263 - IRD 237 – IMBE - Pôle de Recherche Agro environnementale de la Martinique
(PRAM-IRD) B.P. 214 Petit Morne, 97232, Le Lamentin, Martinique.
[b]UPR Fonctionnement Systèmes de cultures bananes plantains et ananas, CIRAD/PRAM
B.P. 214 Petit Morne, 97232, Le Lamentin, Martinique
[c]Cirad/PRAM, UPR fonctionnement agroécologique et performances des systèmes de culture
horticoles, B.P. 214 Petit Morne, 97232, Le Lamentin, Martinique.

thierry.woignier@imbe.fr

Chlordecone (CHLD) is an organochlorine insecticide, used in order to control a wide range of pests in tropical countries. This acutely toxic molecule still persists in the soil and contaminates crops, water resources and ecosystems. All soils are not equivalent in terms of CHLD contamination and in their ability to transfer the pollutant to water and to plants. Andosols are generally more polluted than the other kinds of tropical soils but preliminary results suggest that andosols release less CHLD to percolating water and crops than usual soils. Andosols contain amorphous clays (allophane) which present unique structures and physical properties compared to usual clays. Allophanes are amorphous alumino silicate, the unit cell appears as hollow spheroids with diameter between 3 and 5 nm. These alumino silicates have a high pore volume (~ 70%) and develop a specific surface area as high as 700 $m^2.g^{-1}$. On a structural point of view, scattering data demonstrate that allophane aggregates have fractal geometry and the structure of allophane aggregates can be described by clustercluster aggregation. In conclusion, allophane aggregates have physical features very close to that of synthetic gels: large pore volume and water content, a broad pore size distribution, a high specific surface area and a fractal structure.

Our study hypothesizes that allophane microstructure favor pollutants accumulation in soils. The purpose of this study is to put forth the importance of the fractal microstructure, the associated tortuous interface and large specific surface area for pollutant trapping in soil. We characterize the fractal structure of the allophane aggregates at the nano scale by small angle x-rays scattering and electronic microscopy. We calculate that the main part of the pore volume and porous surface in these clays is due to the allophane fractal structure. We propose that the large porous surface and the low transport properties in allophane aggregate could explain the lesser CHLD release in environment. The fractal and tortuous microstructure of the allophane aggregates plays the role of a labyrinth which fix and traps the pollutant.

PB39

THE ADSORPTION OF CU(II) CATIONS BY THE SURFACE-SILYLATED DIATOMITE (DIATOMACEOUS EARTH) AND THE EFFECTS OF HEATING ON THE SURFACE SILYLATION

Yuan Peng,[1]*, Liu Dong [1], Liu Kangkang[2], Zhong Yuanhong[1,3], Tan Daoyong [1,3]

[1] Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences, Guangzhou 510640, China.
[2] School of Materials Science and Engineering, Jiangsu University of Science and Technology,
Zhenjiang 212003, China.

yuanpeng@gig.ac.cn

The calcined diatomite was previously supposed to be structure-destroyed or at least surface-reconstructed so that unsuitable for surface silylation for the purpose of adsorption. In the present work, various chemical, spectroscopic (Fourier transform infrared spectroscopy, thermogravimetry, and X-ray photoelectron spectroscopy) and microscopic (scanning electron microscopy and transmission electron microscopy) characterization techniques were combined to study the key mechanism about how the evolution of the hydration state of diatomite under heating influences the organosilane functionalization process. γ-aminopropyltriethoxysilane (APTES, $H_2NCH_2CH_2CH_2Si_4(OCH_2CH_3)_3$) was used for the silylation of diatomite. This study indicates surface silylation of diatomite is achievable even for diatomite calcined at high temperature, and the interface interactions between the hydroxyl species of diatomite and APTES are strongly affected by heating pretreatment. Physically adsorbed water was largely preserved in diatomite at a low heating temperature, leading to the strong hydrolysis of APTES and the subsequent oligomerization
between the hydrolyzed APTES. Under heating at high-temperature (800 °C), the isolated silanols initially covered by water molecules were exposed and available for the direct grafting of APTES, forming a grafting-dominant structure with high thermal stability (540 °C). The Cu(II) adsorption (18.5 mg/g) on the APTES-modified diatomite are at least 13 times greater than that on the unmodified one because of the high affinity of the amino groups for Cu ions. The grafting-dominant modified diatomite has dramatically higher efficiency for Cu(II) adsorption than the oligomerization-dominant one. These fundamental results demonstrate that the commercially calcined diatomite product is capable of being used for silylation. For the metal adsorption purpose, the heating temperature of a given diatomite must be carefully selected to generate a grafting-dominant silylation.

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SESSION C:

Interfacial processes in the environment: adsorption, aggregation, speciation, (bio)adhesion.

IC1

HUMIC ACIDS: DISSOLUTION AND ADSORPTION KINETICS

Koopal Luuk K.*

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen,
The Netherlands.

luuk.koopal@wur.nl

Humic Acids (HAs) are important aquatic and soil biomaterials. HA nano-particles are structured by physical and chemical interactions and contain aromatic and aliphatic structures and a range of carboxylic and phenolic groups that can dissociate and charge the particles. The charge is governed by the pH and very important for HA dissolution and HA adsorption on mineral particles. HAs are soluble in alkaline solutions and aggregate and precipitate in acid solutions whereas their adsorption to mineral particles is very prominent in mildly acid solutions and small in alkaline solutions. Apart from the equilibrium state the kinetics of dissolution and adsorption are important. Knowledge of dissolution and desorption kinetics are relevant for the alkaline extraction of soil HAs, for the fate of HAs in natural systems and for laboratory studies of HAs.

The dissolution rate of dried HA particles under stirred conditions and 25° C is measured by UV absorbance [1]. The rate is very slow at pH 4 and may take several years to achieve complete dissolution. Increasing the pH increases the rate and at pH 11 complete dissolution is achieved within 30 min.

Short-time adsorption/desorption kinetics of HA on optically smooth oxide surfaces is measured by stagnation point flow reflectometry at 25° C [2]. Long-time HA adsorption kinetics and equilibrium adsorption are studied by depletion from solution using iron oxide suspensions [3]. The rate of adsorption of humic acid on iron oxide and the equilibrium adsorption decrease with increasing pH. Desorption upon dilution at constant pH is slow and can hardly be achieved. Since there is no change in pH the interactions in the adsorbed layer remain unchanged and the only driving force for desorption is the decrease of the humic acid concentration in solution and this effect is insufficient for desorption. Desorption of HA, adsorbed at low pH, by increasing the pH (either at constant HA concentration, or without HA in solution) is fast and reversible. The rate increases with increasing pH, due to increasing electrostatic repulsion.

Long-term kinetic polydisperity effects of adsorption are studied with the depletion method. In time large HA molecules replace the readily adsorbed, small, HA (or Fulvic Acid; FA) molecules. Preferential adsorption of large HA molecules over small HA (or FA) molecules leads to a rounded shape of the adsorption isotherm. The 'roundness' of the isotherm increases with decreasing pH. The adsorption/desorption hysteresis upon desorption by dilution is due to adsorption fractionation, not to irreversible adsorption.

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RC1

ADSORPTION OF METHYLENE BLUE BY HUMIC ACID-COATED FE_3O_4 NANOPARTICLES

Zhang X.[1], Zhang P.[2]*, Wu Z.[2], Zeng G.[2]*,Zhou C.[3]

[1] College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China.
[2] Key Laboratory of Environmental Biology and Pollution Control (Ministry of Education), Hunan University, Changsha 410082, China.
[3] College of Science, Hunan Agricultural University, Changsha 410128, China.

Correponding author

A novel low-cost and facile synthesis of magnetic nano-sorbent was developed with co-precipitation of humic acids and Fe_3O_4 nanoparticles (HA-Fe_3O_4)[1]. TEM analysis showed roughly spherical shapes of HA-Fe_3O_4 core with an average diameter of about 15 nm. TGA characterization (Figure 1a) showed the HA-Fe_3O_4 nanoparticles contained about 50% (w/w) HA. FIRT spectra (Figure 1b) showed characteristic absorption of HA at 1604 cm^{-1} and 1701 cm^{-1}, which was attributed to C=O bond stretching vibration in carboxylic salt and free carboxylic acid respectively. The HA-Fe_3O_4 exhibited typical superparamagnetic characteristics with a saturation magnetization of 77emu/g, which make solid-liquid separation easily by an external magnet[2].

The HA-Fe_3O_4 nanoparticles were applied for Methylene blue (MB) adsorption. Results showed that the HA-Fe_3O_4 nanoparticles had much higher adsorption capacity than bare Fe_3O_4 and HA powders. The structure of the HA-Fe_3O_4 nanoparticles was stable in a broad pH range of 3-11. The $t_{1/2}$ corresponding to 50% of adsorbed MB was calculated to be 7 min, and the adsorption kinetics can be described by pseudo-second-order equation. The sorption isotherms of HA-Fe_3O_4 agreed well with Langmuir sorption model and the maximum adsorption capacity was 0.291 mmol/g. Electrostatic and complex adsorption may be the main sorption mechanisms for MB adsorption onto HA-Fe_3O_4. Desorption and recycling of the HA-Fe_3O_4 nanoparticles were also done easily by a mixed solution with a volume ratio of methanol to acetic acid of 9:1.

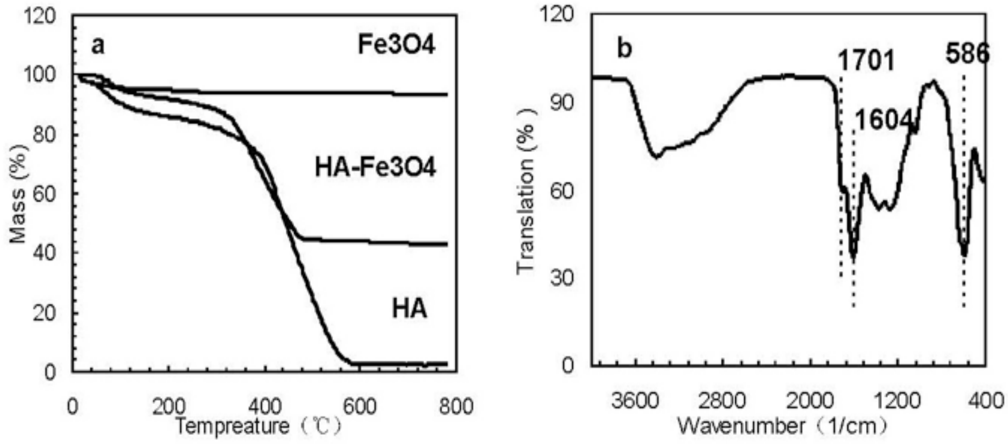

Figure 1 TGA curves (a) and FTIR spectra (b) of the magnetic HA-Fe_3O_4 nanoparticles

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RC2

THE INTERACTION BETWEEN HUMIC ACID AND ALUMINIUM COAGULANTS AT DIFFERENT pH VALUES

Yu Wen-Zheng [1] and Gregory John[2]*

[1] State Key Laboratory of Environmental Aquatic Chemistry, Chinese Academy of Sciences, Research Center for Eco-Environmental Sciences, Beijing 100085, China.
[2] Department of Civil, Environmental and Geomatic Engineering, University College London, Gower Street, London WC1E 6BT, UK

j.gregory@ucl.ac.uk

Humic substances are found in many natural waters and need to be removed during water treatment. One common method is by the use of hydrolysing coagulants, such as Al and Fe(III) salts. Pre-hydrolysed coagulants such as polyaluminium chloride (PACl) are also widely used. The mode of action of these additives depends greatly on pH. At low pH, coagulation occurs because of charge neutralisation of the humics by cationic hydrolysis products. With increasing pH, hydroxide precipitates are formed, which can adsorb humic substances and hence give efficient removal by physical separation methods.

In the present work, emphasis is on the removal of humic acid by precipitates formed from two forms of Al coagulant: aluminium sulphate ("alum") and a PACl sample prepared by slow neutralisation of an $AlCl_3$ solution to give a B (OH/Al) value of 2.5. The latter product, designated $PACl_{25}$, contains more than 90% of the tridecameric form, "Al_{13}". These coagulants were used to treat solutions of a commercial humic acid over a range of pH values. The degree of removal of humic acid was assessed by measuring the decrease in UV absorbance. Residual Al levels were measured by ICP atomic emission spectroscopy.

At around neutral pH, both coagulants were very effective, but $PACl_{25}$ gave good removal over a much broader pH range than for alum. In acidic solutions this was ascribed to the higher charge of Al_{13} species, giving more effective charge neutralisation. The optimum pH for alum was around 6, corresponding to the minimum Al solubility, where adsorption on the amorphous precipitate would be most effective. Over the pH range 7 – 9 alum showed a marked loss of effectiveness, which was closely correlated with an increase of residual Al (i.e. a loss of precipitate). By contrast, $PACl_{25}$ showed much less residual Al, even up to pH 11, indicating a significant difference between the precipitates from the two coagulants. The removal of humic acid was also much better than for alum at high pH.

It was shown that, for both coagulants, precipitates aged for periods up to 20 minutes were less effective in removing humic acid than fresh precipitates. Such loss of activity of hydroxide precipitate surfaces on aging has been observed previously, for instance by the reduction of adsorption capacity for phosphate [1]. It may be that this effect also plays a part in limiting the re-growth of broken hydroxide flocs [2] Also, higher stirring rates gave better removal of humic acid because smaller flocs were formed with a correspondingly higher effective surface area.

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CHARACTERIZATION OF HUMIC ACID REACTIVITY MODIFICATIONS DUE TO ADSORPTION ONTO α AL$_2$O$_3$

Benedetti M. F.[1]*, Janot N.[1,2], Zheng X.[3], Croué J.P.[3] , Reiller P. E.[2]

[1]Université Paris Diderot, Sorbonne Paris Cité, Institut de Physique du Globe de Paris, UMR 7154 CNRS, F-75013 Paris, France,
[2] CEA/DEN/DANS/DPC/SECR, Laboratoire de Spéciation des Radionucléides et des Molécules, F- 91191 Gif-sur-Yvette, France
[3]King Abdullah University of Science and Technology Thuwal, Water Desalination and Reuse Research Center, Kingdom of Saudi Arabia.

benedetti@ipgp.fr

Adsorption of purified Aldrich humic acid (PAHA) onto α-Al$_2$O$_3$ is studied by batch experiments at different pH, ionic strength and coverage ratios R (mg of PAHA by m^2 of mineral surface). After equilibration, samples are centrifuged and the concentration of PAHA in the supernatants is measured. The amount of adsorbed PAHA per m^2 of mineral surface is decreasing with increasing pH. At constant pH value, the amount of adsorbed PAHA increases with initial PAHA concentration until a constant pH-dependant value is reached. UV/Visible specific parameters such as specific absorbance SUVA254, ratio of absorbance values E2/E3 and width of the electron-transfer absorbance band ΔET are calculated for supernatant PAHA fractions of adsorption experiments at pH 6.8, to have an insight on the evolution of PAHA characteristics with varying coverage ratio. No modification is observed compared to original compound for R ≥ 20 mgPAHA/g. Below this ratio, aromaticity decreases with initial PAHA concentration. Size-exclusion chromatography - organic carbon detection measurements on these supernatants also show a preferential adsorption of more aromatic and higher size fractions.

Spectrophotometric titrations were done to estimate changes of reactivity of supernatants from adsorption experiments made at pH ≈ 6.8 and different PAHA concentrations. Evolutions of UV/Visible spectra with varying pH were treated to obtain titration curves that are interpreted within the NICA-Donnan framework. Protonation parameters of non-sorbed PAHA fractions are compared to those obtained for the PAHA before contact with the oxide. The amount of low-affinity type of sites and the value of their median affinity constant decrease after adsorption. From PAHA concentration in the supernatant and mass balance calculations, “titration curves” are obtained and fitted for the adsorbed fractions for the first time. These changes in reactivity to our opinion could explain the difficulty to model the behavior of ternary systems composed of pollutants/HS/mineral since additivity is not respected.

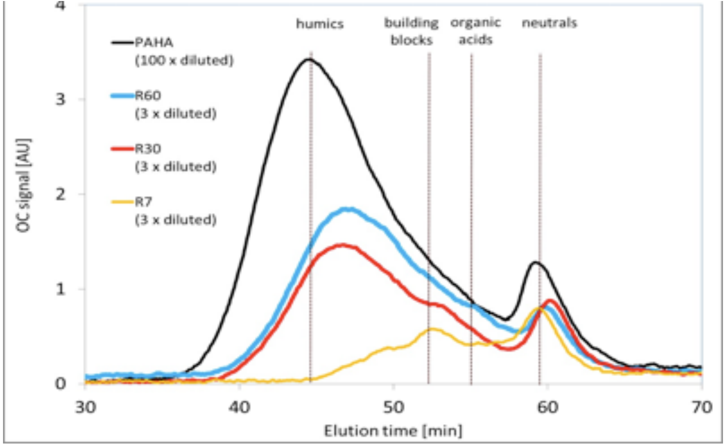


Figure 1: LC-OCD chromatograms of PAHA and of supernatants from adsorption experiments at 0.1M and pH ≈ 6.8 (R in mgPAHA/g α-Al$_2$O$_3$).

KC1

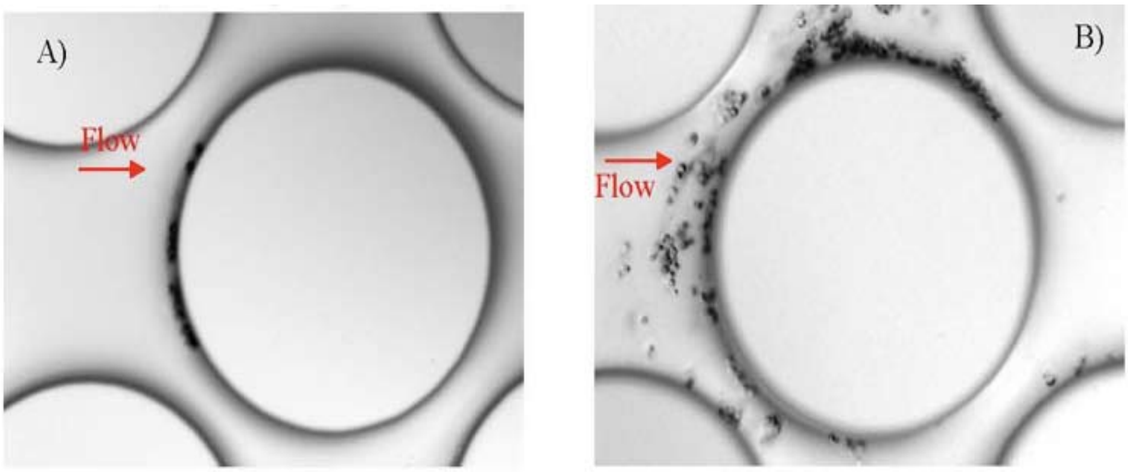
TRANSPORT OF BIOCOLLOIDS IN A SILICON MICROMODEL

Nguyen Thanh H.[1]*, Liu Yuanyuan[1], Lu Nanxi[1], Zhang Changyong[2]

[1]Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign,
Urbana IL 61801
[2]Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland WA 99354

thn@illinois.edu

Effective removal of biocolloids such as bacteria and oocysts by granular filtration requires the knowledge of biocolloid transport and deposition mechanisms, which can be obtained based on real time microscopic observation of transport in porous media. Attachment of *Cryptosporidium parvum* oocysts and *Azotobacter vinlandeii* strains with and without flagela to silica surface in a radial stagnation point flow (RSPF) cell and in a micromodel, which has 2-dimensional (2-D) microscopic pore structures consisting of an array of cylindrical collectors, was studied and compared. Real time transport of oocysts and bacteria in the micromodel was recorded to determine the attached oocyst and bacteria distributions in transversal and longitudinal directions. In the micromodel, oocysts and bacteria attached to the forward portion of clean collectors, where the flow velocity was lowest (see figure below). After initial attachment, oocysts and bacteria attached onto already attached biocolloids (oocysts or bacteria). As a result, the collectors ripened and the region available for flow was reduced. Results of attachment and detachment experiments suggest that surface charge heterogeneity allowed for oocyst attachment.



We further fabricated micromodel with iron-oxide coated collectors to prove that surface charge heterogeneity controls oocyst attachment. Distribution of oocysts on porous media at 100 mM NaCl, pH 7.0-7.2. On clean collector, oocysts (A) attached to the forward portion of the collector. When the surface was covered by oocysts, oocysts (B) were able to attach to already attached oocysts. Experimental condition: porous media depth = 21.3 µm, flow rate = 0.60 mL/hr.

RC4

DESIGN AND PHYSICOCHEMICAL PROPERIES OF THERMO-RESPONSIVE COPOLYMER FILMS FOR APPLICATIONS IN MARINE ENVIRONMENTS

Zimmermann R.[1]*, Duval J. F. L.[2], Cordeiro A. L.[1], Werner C.[1,3]

[1] Leibniz Institute of Polymer Research Dresden, Max Bergmann Center of Biomaterials
Dresden, Hohe Strasse 6, 01069 Dresden, Germany.
[2] LEM, Nancy-Université, CNRS UMR 7569, 15 avenue du Charmois, B.P. 40, 54501
Vandoeuvre-lès-Nancy, cedex France.
[3] Technische Universität Dresden, Center of Regenerative Therapies Dresden, Tatzberg 47, 01307 Dresden, Germany.

zimmermn@ipfdd.de

The control of bioadhesion is of crucial importance in various fields such as the design of implant materials, food processing, or coatings for marine technology and ship hulls. Here we report on the design, detailed characterization, and surface adhesion tests of a novel thermo-responsive polymer film with a transition temperature tuned to fit applications related to the control of biofouling in marine environments. The copolymer consists of poly(N-isopropylacrylamide) (PNIPAAm) and N (1 phenylethyl) acrylamide (PEAAm) and was immobilized as a thin film onto Teflon® AF surfaces using a low pressure argon plasma treatment. The temperature dependent physicochemical properties of the thermo-responsive film were thoroughly characterized and the impact of sea water on the film properties was investigated. It was shown that the immobilized film exhibits a reversible swelling / deswelling with temperature. Inverse contact angles were measured using captive air bubbles and analysed by axisymmetric drop shape analysis to study the wettability of the hydrated thin films at different temperatures. Streaming current measurements performed above and below the transition temperature of the thermo-responsive hydrogel film (at 22°C and 4°C, respectively) indicated that the charging of the polymer / aqueous solution interface is mainly determined by the preferential water ion adsorption at the Teflon® AF surface. The data of the streaming current measurements were further analyzed applying a recently introduced theory for the electrokinetics at diffuse soft interfaces [1]. The theory successfully reproduces the electrokinetic data for the P(NIPAAm-co-PEAAm) copolymer film at 22°C and 4°C over the whole range of pH and ionic strength examined. It was found that the threefold increase of the hydrogel film thickness with decreasing temperature from 22°C to 4°C (*i.e*. from 23 to 70 nm as measured by ellipsometry) is accompanied by an increase of the hydrodynamic penetration length (1/λo)) by a factor of ~1.6. It is demonstrated that this behaviour is in line with a homogeneous distribution of the polymer segments and a homogeneous swelling of the film. Finally we show how the adhesion of the diatom Navicula perminuta is influenced by the film properties at different temperatures.

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RC5

EFECT OF DUAL POROSITY ON COLLOIDAL TRANSPORT UNDER SATURATED AND UNSATURATED FLOW CONDITIONS

Lamy E.[1]*, Lassabatere L.[2], Béchet B.[3] and Andrieu H.[3]

[1] Université de Technologie de Compiègne/Ecole supérieure de chimie organique et minérale (UTC/ESCOM), EA 4297 TIMR, BP 20529, F-60205 Compiègne Cedex, France.
[2] Université de Lyon; UMR5023 Ecologie des Hydrosystèmes Naturels et Anthropisés; Université Lyon 1; ENTPE; CNRS; 3, rue Maurice Audin, 69518 Vaulx-en-Velin, France.
[3] PRES LUNAM, French Institute of Science and Technology for Transport, Development and Networks (IFSTTAR), Department of Geotechnics, Water and Risks, Centre de Nantes, Route de Bouaye CS4, Bouguenais, F-44344, France

edvina.lamy@utc.fr

There is a considerable ongoing effort aimed at understanding the transport and deposition behaviour of colloidal particles in granular porous media. As many contaminants occur as colloids or are associated with colloids, the understanding of the transport and fate of colloidal particles is required to accurately assess contaminant potential and extent, and then to efficiently protect groundwater and soils from contamination. Colloid transport in porous media is a complex phenomenon involving several processes (such as advection, dispersion, Brownian diffusion and release and capture onto the solid surfaces), which depend on different factors. Many previous studies were focused on the physico-chemical factors that could influence colloid transport and retention in homogenous porous medium. However, much less information is available on the colloid transfer processes occurring in heterogeneous porous media. Moreover, studies are often restricted to saturated systems and the ability to predict the fate of colloids in the vadoze zone is currently limited by the incomplete understanding of the deposition mechanisms.

The aim of this study was to investigate the influence of water content and porosity of granular medium (dual versus single porosity) on the transport of hydrophilic latex particles.

Miscible displacement experiments were carried out under saturated and unsaturated flow conditions in laboratory model systems (single-porosity sand and dual-porosity granular medium) under steady state flow conditions. Solute and colloid transport was simulated considering physical nonequilibrium for flow along with a first order sink term for colloid retention, implemented in HYDRUS 1D code. Colloidal retention was highly dependent on the soil porosity with a higher retention in the dual-porosity gravel compared to the singleporosity sand (32 to 92% in mass depending on the physically porous medium heterogeneity and the degree of water saturation). In comparison to sand, the intra porosity of gravel particles was responsible for additional trapping of colloids. Yet, tracer experiments showed that flow was more heterogeneous in the gravel medium. Indeed, colloid retention was not optimal since the colloids mainly passed through the preferential flow pathways, avoiding the zones most favorable for trapping (i.e. intra particle porosity). The addition of an intraparticle porosity made the flow pattern more heterogeneous, the colloid transport more complex, but the colloid trapping through physical straining more efficient.

RC6

FLOCCULATION OF SUSPENSIONS BY POLYELECTROLYTE MIXTURES AND ITS USE IN WATER TREATMENT

Bárány S.

University of Miskolc, Faculty of Healthcare, 3515 Miskolc-Egyetemvaros, Hungary

akmbsab@uni-miskolc.hu

Polymers are widely used as flocculants for suspensions in many industrial applications, such as mineral processing, papermaking, water treatment and biotechnology. In recent years there has been considerable interest in the use of multi-component flocculants, especially dual-polymer systems. In the latter case, there can be significant advantages over the use of single polymers.

In order to elucidate the mechanisms of flocculation by polyelectrolyte (PE) mixtures, we have studied the effect of adsorption of cationic and anionic PEs as well as their binary mixtures on the electrokinetic potential, kinetics of aggregation, size and strength of flocs formed from polystyrene, silica, kaolin and bentonite particles as a function of the polymer dose, charge density (CD) of the polyelectrolyte, mixture composition, sequence of the components addition and intensity of stirring the system. Flocculation experiments were performed in a flow system using a Photometric Dispersion Analyzer PDA-2000. Electrokinetic potential of particles was measured by Brookhaven zeta-sizer instrument. The adsorbed amount of polymers was determined from the change of the PE concentration prior and after adsorption; the latter was measured using colloidal titration with surfactant.

It is shown that maximal aggregation of suspension particles occurs at polymer content of about 0.5-1.5 mg/g that is approximately an order of magnitude less than the concentration corresponding to the plateau value of adsorption for cationic polymers and two-three times less than the maximal adsorption of anionic polymers.

A synergism in flocculation capacity in mixtures of moderate and weakly charged polyelectrolytes was observed. Mixtures of medium/low charged anionic polyelectrolytes and medium or low charged cationic flocculants gave optimum flocculation at mass ratios, corresponding to many-fold excess of negative charges over positive ones in the adsorbed layer. Deviation from the optimum composition gave slower flocculation and significantly smaller floc sizes. An initial intensive short stirring the suspension accelerates the aggregation process and increases the size of flocs independently of the sequence of polymers addition. In mixtures of cationic and anionic polyelectrolytes, whatever the sequence of addition, the particles acquire ζ-potential that is typical for particles bearing only anionic polyelectrolyte. The laws observed were explained by features of polyelectrolytes conformation in adsorbed mixed polymer layers.

Examples on the application of dual polymers in purification of municipal wastewaters, recycled and wastewaters of coal processing, in papermaking and wastewater sludge treatment are given.

The author thanks Dr. R. Meszaros, for performing flocculation experiments and Prof. J. Skvarla for providing the zeta-sizer instrument and useful discussions.

Also I express my deep gratitude to Prof. David Waite, University of New South West, Sydney, Australia, for financial support of my participation in the IAP conference.

RC7

INITIAL STAGE DYNAMICS OF FLOCCULATION OF PSL PARTICLES INDUCED BY AN EXCESS ADDITION OF POLYELECTROLYTES UNDER HIGH IONIC STRENGTH

Adachi Y.* and Xiao J.

Graduate School of Life and Environmental Sciences, University of Tsukuba, Japan

yas@ sakura.cc.tsukuba.ac.jp

Initial stage dynamics of colloidal flocculation induced by cationic polyelectrolyte was studied under high ionic strength in order to evaluate the possible effective layer thickness of adsorbing polyelectrolyte on the colloidal particles. Due to high ionic strength, charges in polyelectrolyte chains are shielded, so that the chains will take conformation of random coils. The size of polyelectrolyte in the solution, ap, was evaluated by the viscometry and by dynamic light scattering (DLS). Normalizing method of end-over-end rotation was adopted to analyze the initial-stage dynamics of flocculation. Drimethylamino ethylmethacrylates with nominal molecular weights of 4.9 million and 2.0 million were tested as flocculants. The progress of flocculation was monitored by counting the number concentration of colloidal particles, N(t)1/cm^3. By the excess addition of polyelectrolytes, the rate of flocculation just alter the start of mixing was remarkably enhanced from that of salt-induced rapid coagulation. However, the progress of flocculation essentially stopped after short period from the start of mixing operation, implying saturation of adsorption. It is this short period that the protruding length of polyelectrolyte attached to the surface of colloidal particle, δHe, was evaluated from the enhancement of the rate of flocculation. δHe, was confirmed to be several times larger than the size of polyelectrolyte in bulk solution determined by viscometry and DLS. This result was interpreted that the elongation of polyelectrolyte chain induced by hydrodynamic force in the mixing flow. This elongation of polyelectrolyte chain issignificant in the flocculation by polyelectrolytes.

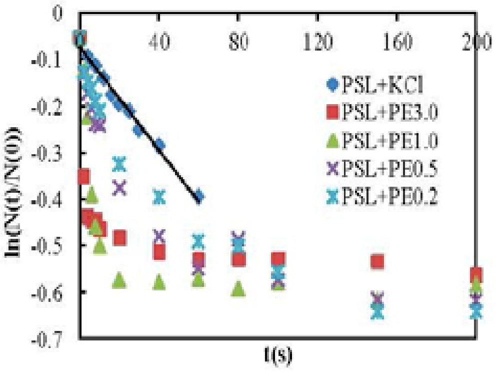

Fig.1 ln(N(t)/N(0)) vs. t, for flocculation with polyelectrolyte (Mw=4.9 •106 [g/mol]). The number of steps(t) up to 200 steps. PE3.0 denotes 3.0 ppm polyelectrolyte concentration.

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KC2

ADSORPTION OF METAL-BASED NANOPARTICLES: THE IMPORTANCE OF SURFACE MODIFICATION FROM SIMPLE TO COMPLEX ORGANICS

Lau B.L.T.[1,2], Ikuma K.[1], Bovet N.[2], Huang R.[1] Furman O.[1], Stipp S.L.S.[2]

[1] Department of Geology, Baylor University, Waco, Texas, USA
[2] NanoGeoScience Group, NanoScience Center, University of Copenhagen, Denmark

boris_lau@baylor.edu

Sorption of nanoparticles (NPs) on different environmental surfaces has important implication on their fate and transport in aquatic systems. With the use of surfacesensitive/nano-scale tools (e.g., quartz crystal microgravimetry, atomic force microscopy, and X-ray photoelectron spectroscopy), we focused to better understand the adsorption kinetics and the nature of interactions as NPs approach surfaces coated with selfassembled monolayers (SAMs) and natural organic matter (NOM). While SAMs provide structurally well-defined functional groups at surfaces for better mechanistic understanding, NOM-coated substrates reflect the surfaces that the NPs are likely to encounter in relevant environmental conditions. Regarding lead sulfide NPs (PbNPs), we examined the effects of four SAMs as substrate surfaces on the adsorption kinetics of 10 nm PbNPs. The highest rate of adsorption was observed on surfaces modified with a hydrophobic SAM at pH 6 and 10 mM NaCl. PbNPs adsorbed onto three hydrophilic SAMs (negatively, positively, and neutral-charged) at rates that were 22%, 31%, and 1.4% of the rate observed with hydrophobic SAM, respectively. These results suggest that various chemical features of the substrate surface including hydrophobicity and charge impact PbNP adsorption.

Regarding iron oxide NPs (FeNPs), experiments were conducted to study the immobilization of two different sizes of FeNPs onto substrate modified with two hydrophilic SAMs. It is shown that the extent and rate of FeNPs adsorption onto substrate surfaces can be modulated electrostatically. Control over the surface coverage of the adsorbed FeNPs has been demonstrated by pH variation. Size-dependent adsorption kinetics was observed, with the 79-nm FeNPs adsorbed 2 to 3 times faster than the 116- nm FeNPs.

Regarding silver NPs (AgNPs), we evaluated the relative impacts of different NOM fractions (humic acid (HA) and fulvic acid (FA)) on the adsorption kinetics of 50 nm citrate-stabilized AgNPs onto silica surfaces. At pH 8 and 1 mM $Ca(NO_3)_2$, the rate and extent of uncoated AgNP adsorption changed due to substrate modification. After silica substrates were coated with HA and FA, the adsorbed mass of AgNPs decreased by ~35% and ~60% respectively. There was no observable adsorption when AgNPs and substrate were both coated with HA. However, FA-coated AgNPs adsorbed significantly onto FA coated substrate. These results suggested that HA and FA exert different influences on the fate and transport of AgNPs.

Overall, our findings highlighted the critical role of surface modification in NP substrate interactions. These findings are important in the future design of NPs to ensure successful applications as well as the environmental health and safety of NPs.

RC8

RESTRUCTURING OF ORGANIC COATINGS UPON DRYING: CONSEQUENCES FOR THE ACCESSIBILITY OF SORPTION SITES

Krüger J.[1]*, Lang F.[2]

[1] Chair of Soil Science, Department of Ecology, Berlin Institute of Technology, Berlin, Germany
[2] Institute of Soil Science and Forest Nutrition, Faculty of Forest and Environmental Science,
Albert-Ludwigs University Freiburg, Freiburg i.Br., Germany

jaane.krueger@tu-berlin.de

Surface chemical and structural properties of biogeochemical interfaces (BGIs) determine sorptive interactions of organic pollutants in soils. Under environmental conditions BGIs may be subjected to moisture fluctuations. Effects of drying on the surface properties and resulting sorptive interactions are in the centre of our study.

We hypothesise that (i) drying of organo-mineral associations in presence of monovalent cations induces a collapse of organic macromolecules and thus a more positive zeta potential and that (ii) polyvalent cations function as "structure stabilisers" thereby reducing the "drying-effect" on the zeta potential of organo-mineral associations. We expect that (iii) the sorption of polar organic substances is controlled by the zeta potential of organo-mineral associations according to electrostatic interactions, while the sorption of nonpolar organic substances decreases with increasing absolute value of the zeta potential.

To test our hypothesis we measured the zeta potential of polygalacturonate (PGA) coated lepidocrocite colloids without drying and after air-drying and rewetting. We conducted the experiments in presence of 10 mmol L^{-1} K^+ (pH 5 and 4) and Al^{3+} (pH 4). Additionally we conducted sorption experiments with ^{14}C-labeled MCPA and phenanthrene to the differently treated material.

As expected the zeta potential of mineral-organic associations got more positive upon drying. However, the shift towards more positive zeta potential was similar for K^+ and Al^{3+} saturated samples.

In sorption experiments no clear relation between zeta potential and amount of sorbed MCPA was found. Yet we observed strong adsorption of MCPA to Al saturated samples, which clearly decreased upon drying. We propose that this may be due to different sorption mechanisms of MCPA to wet and re-wetted BGIs: In the wet state Al^{3+} cations are accessible and MCPA is bound by inner sphere complexes. After drying the collapsed PGA-network buries Al^{+3} cations and unspecific MCPA sorption at mineral surfaces may become the predominant process. Recently we are testing this assumption using thermocalorimetric analyses. The hydrophobic phenanthrene showed significantly higher affinity to re-wetted samples than to samples, which had not been dried. Drying of the PGA-network may increase its hydrophobicity and may thereby increase hydrophobic interactions.

We conclude that restructuring of organic coatings upon drying may decrease the accessibility of ionic sorption sites of organo-mineral associations and change the predominant sorption mechanism. Thus drying of BGIs is crucial not only for the sorption capacity but also for the sorption mechanism of organic pollutants.

RC9

SORPTION OF BORATE ON CALCINED PRODUCTS OF NATURAL DOLOMITE: EFFECT OF CALCINATION TEMPERATURES

Sasaki K.* Hosomomi Y., Qiu X., Hirajima T.

Department of Earth Resources Engineering, Kyushu University

keikos@mine.kyushu-u.ac.jp

Boron is a dynamic trace element that can affect the metabolism or utilization of numerous substances involved in life processes, and also one of the most difficult elements to immobilize in aquatic environments [1]. Natural dolomite from Ogano (Japan) was modified to provide as a sorbent for borate. Calcination condition was investigated at 700ºC ~900ºC under air and Ar atmosphere including 1% H_2.

Calcite ($CaCO_3$) and magnesian calcite $(Ca,Mg)CO_3$ were included as impurities as well as dolomite ($CaMg(CO_3)_2$) in the specimen. Increasing with calcination temperature, sequential de-carbonation was confirmed by XRD, that is, transformation of dolomite into magnesia and calcite at 700ºC, transformation of magnesian carbonate into magnesia and calcite at 800ºC, and transformation of calcite into lime at 900ºC. Surface molar ratio of Ca/Mg decreased from 1.6 to 0.6 by calcination at more than 700ºC. Sorption isotherm of borate at 25ºC was compared with calcined products under different conditions. In calcination under air, the greatest sorption density of borate was found with calcined product at 700ºC. BET type of sorption isotherm curve suggests that removal of borate is expected to occur through destructive sorption of MgO in calcined products. Under reducing conditions the greater sorption density was observed than under the air. Removal mechanism of borate is principally co-precipitation with $Mg(OH)_2$ in hydration of MgO. The above result suggests the surface of magnesia (MgO) was more significantly affected by CO_2 in a process of de-carbonation at higher temperature, and that higher crystalinity of MgO is more reactive in hydration.

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(2011) J. Hazard. Mater., 2011, 185, 1440.

RC10

MODELLING As(V) SORPTION BEHAVIOR ON NATURAL AND PURIFIED ILLITE

Campredon B.[1], Hurel C.[1], Lützenkirchen J.,[2] Marmier N.[1]*

[1] Ecomers - Science of Faculty, University of Nice Sophia Antipolis, Parc Valrose, 28 avenue Valrose, 06108 Nice cedex 2 France

[2] Institut für Nukleare Entsorgung, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

marmier@unice.fr

The adsorption behavior of As(V) onto natural and purified illite from the Puy-en-Velay (France) was investigated as a function of ionic strength, pH, and arsenic initial concentration. Natural and purified illite surfaces were previously characterized by DRX, FTIR, and by potentiometric titrations. DRX and FTIR results have demonstrated that the natural illite sample contained a high amount of calcite impurities that could explain large discrepancy between the experimental results obtained for the natural and the purified illite sample. Indeed, arsenate sorption onto natural illite increases with alkalinity, while sorption onto purified illite exhibits a maximum at acidic pH and then decreases with increasing pH. Characterization experiments and sorption data illustrate that after treatment (based on nitric acid washing) the calcite impurities were negligible.

The shell optimization Universal CODE (UCODE) was used in combination with a modified version of FITEQL2.1 run in simulation mode (i.e. as an application called by UCODE) to fit (i) the potentiometric titrations to determine the acid-base parameters of illite and (ii) the adsorption data to determine the adsorption stoechiometries of As(V) on illite and the concomitant stability constant. The Basic Stern electrostatic model (BSM) and the 2-pK surface complexation model were considered in the calculations. The best fit between experimental and calculated data was obtained when three monodentate arsenate species at the edge sites of the purified illite sample were considered. A good fit was obtained between calculated and experimental data for the natural illite, by adding to the previous equilibriums competition of dissolved carbonates with As(V) at the edge sites of illite.

The model was able to describe the adsorption behavior of As(V) on both natural and purified illite by considering one kind of edge site (aluminol sites) and 3 surface complexes, and competitive adsorption of dissolved carbonates on aluminol sites.

RC11

REACTIVITY OF COLLOIDAL SUSPENSIONS OF ORGANICALLY MODIFIED SILICA TOWARD METAL IONS, KINETICS AND THERMODYNAMIC ASPECTS

Hébrant M.*, Rose Hélène M., Walcarius A.

University of Lorraine, LCPME, UMR CNRS-UL n°7565, ELAN, 54600 Villers-lès-Nancy, France

marc.hebrant@lcpme.cnrs-nancy.fr

Studying metal ion extraction by silica colloidal particles bearing a covalently bound highly selective complexing agent is important for at least two reasons:

- From the fundamental point of view, the understanding of the reactivity variation of a given extractant induced by its grafting onto a solid surface is far from being complete. The metal ion dispersion in the environment being conditioned by their adsorption behavior on solid the interest of such studies is obvious.
- From the applied point of view, the development of an alternative efficient extraction process without solvent would be particularly interesting for the treatment of industrial waste waters.

In this work, we investigate the reactivity with copper(II) and nickel(II) of 5-phenyl-azo-8-hydroxyquinoline (5Ph8HQ) grafted on colloidal fumed silicas. The silica considered here have specific surface area of 200 $m^2.g^{-1}$ and 390 $m^2.g^{-1}$. The reaction kinetics is studied by means of the stopped flow technique, one syringe containing a colloidal dispersion of the organomodified silica, the other one a solution of the metal ion. Since an intimate mixing is ensured in such a device, this experimental strategy allows to access to true kinetic data without any hydrodynamic contribution. In such conditions there is no need of empiric model, such as the often used so-called pseudo-second order model.The experimental curves adopt a very particular shape, due to a particular spectrometric behavior of the interfacial complex formed. The observed rates constant are compared to those obtained with the same couple extractant/metal in micellar solution [1].

The thermodynamic extraction data is obtained by using the ultrafiltration technique. The stability of the grafting and of the colloidal suspension is demonstrated. The ionization of the grafted particles is taken into account to calculate the stability constant.

Comparing the stability constants obtained here with those given in the literature for the same ligand grafted on classical silica [2] shows that the colloidal nature of the solid can greatly influence the stability of the formed complex.

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RC12

IMPACT OF IONIC STRENGTH AND RESIN THICKNESS ON METAL ACCUMULATION IN DIFFUSIVE GRADIENTS IN THIN FILMS (DGT)

Puy J.[1]*, Mongin S.[1], Uribe R.[1], Cecilia J.[2], Galceran J.[1], Lin C.[3], Zhang H.[3], Davison W.[3]

[1]Department of Chemistry, [2]Department of Mathematics, Universitat de Lleida, Av. Rovira Roure 191, 25198 Lleida, Spain
[3]Lancaster Environmental Centre, Lancaster University, Lancaster, U.K.

jpuy@quimica.udl.cat

DGT[1] has emerged as a powerful technique for in situ measurement of metal fluxes. It consists of a resin immobilised and embedded in a gel (the resin disc) that strongly binds metal ions which have crossed another hydrogel layer of the same composition (the diffusive gel) on their way from the sample solution.

Partially labile or inert complexes able to diffuse through the diffusive gel are expected to penetrate into the resin layer [2,3]. This penetration and the binding of the free metal by the resin in the resin layer extends the effective reaction layer. Consequently both the metal flux and the lability degree of the complex are increased compared to the values expected when complexes are unable to penetrate into the resin phase. This effect is so important that, at an ionic strength of 100 mM, the main fraction of the metal accumulated in the resin comes from the complex dissociation inside the resin disc.

However, at low ionic strength, the penetration of complexes into the resin disc can be influenced by an electrostatic effect derived from the electrical charges of the resin beads. Negatively charged complexes will experience an electrostatic exclusion leading to a reduction of the accumulated mass.

The mass of cadmium accumulated at different times by commercially available DGT devices deployed in solutions containing Cd at a concentration close to 0.01 mol m^{-3} and NTA at concentrations of 0.249 and 1.8 mol m^{-3} was measured. pH was adjusted to 7 or 7.5 and ionic strength to 0.05 M with $NaNO_3$ (Merck, suprapur). In a second series of experiments, the accumulation of Ni, Co and Cd in the presence of NTA was measured in systems with different concentrations of background electrolyte, $NaNO_3$, covering the range 0.01 mM-100 mM and pH 7.

The analytical prediction of the penetration effect on the metal accumulation matches the results for the Cd NTA system at different pH and NTA concentrations. At low ionic strength, the metal accumulation is reduced, especially for Ni, whose complex with NTA is least labile. As M-NTA complexes carry a negative electrical charge, the reduction of the metal accumulation can be explained by a repulsive effect between the resin and the complex. Analytical expressions derived to take into account this electrostatic effect allow an accurate fitting of the experimental data. This effect is less important for Cd-NTA, due to its labile behaviour.

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RC13

NICKEL (BIO)AVAILABILITY IN ULTRAMAFIC SYSTEMS FROM GOIAS, BRAZIL: AN OVERLOOK OF THE SOIL COMPARTMENTS.

Zelano I.[1,5], Sivry Y.[1]*, Jouvin D.[2], Tharaud M.[1], Quantin C.[2], Gelabert A.[1], Montarges-Pelletier E.[3],
Pichon R.[2], Garnier J.[4], Abollino O.[5] and Benedetti M.F.[1]

[1]UMR 7154, Université Paris Diderot – IPGP, PRES Sorbonne Paris Cite, 35 rue Helene Brion, 75013, Paris, France
[2]UMR 8148 IDES, Universite Paris Sud, Orsay, France
[3]UMR 7569 LEM, CNRS, Vandoeuvre les Nancy, France
[4]Instituto de Geociências, Universidade de Brasilia
[5]Univeristà degli Studi di Torino,Via Pietro Giuria 5, 10125 Torino.

sivry@ipgp.fr

The overall objective of this work is to understand and quantify the Ni availability and mobility in ultramafic soils and ecosystems located in the Goías State (Brazil) and impacted by the mining activity. In this work we quantified the Ni availability and established the link between Ni solid speciation and availability in such a specific (ultramafic) context. Two different techniques were used in parallel to investigate Ni mobility: the Donnan Membrane Technique (DMT) (Jouvin *et al.* [1]), to quantify the free-metal ion in soil suspensions and Isotopic Dilution (ID) to quantify the pool of isotopically exchangeable Ni addressing the kinetic aspect of the exchange in water and soil suspensions (Sivry et al [2]). Samples were spiked with stable ^{61}Ni and isotopic ratio (^{61}Ni/^{58}Ni) were measured with a HR-ICP-MS (Thermo Element II). Data display an isotopically exchangeable pool of Ni (ENi) considerably higher than Ni in solution in some cases: up to 407±3 µg L^{-1} ENi (after 6 days of interaction) and only 46±1 µg L^{-1} for dissolved Ni in Barro Alto samples. The experiment highlighted also the kinetic aspect of the exchanges: after 2 days of interaction, samples from Barro Alto reach about 75% of the total ENi, while up to 99% of ENi pool is already quantified in samples from Niquelândia. This different behavior is directly relied to the different solid speciation of the suspended matter in solution. XRF analysis on solid samples display a content of Ni from 0.6 wt% up to 5.9 wt% in ores, from 0.1 wt% up to 3.2 wt% in sludges and from 0.02 wt% up to 3.8 wt% in soils. XRD results indicate the presence of different phases: in particular goethite, chromite, vermiculite and quartz in soils from Barro Alto, and lizardite, chromite, quarts and hematite in Niquelândia soils.

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RC14

HETEROGENEOUS REACTION OF ACETIC ACID ON MGO, ALPHA-AL_2O_3, AND $CACO_3$ AND THE EFFECT ON THE HYGROSCOPIC BEHAVIOR OF THESE PARTICLES

Ma Q., Liu Y., Liu C., He H.*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing,
100085, China.

honghe@rcees.ac.cn

Mineral aerosol represents one of the largest mass fractions of global aerosols and it is considered as one of the largest uncertainty in predicting future climate change due to its complexity in climate effect. [1] Heterogeneous reaction on the surface of mineral dust has a significant effect on the physicochemical properties of mineral dust, which consequently is one of the most concerned major in atmospheric science. [2]

In this study, the effect of heterogeneous reaction with acetic acid on the hygroscopic behavior of typical mineral particles, including Al_2O_3, $CaCO_3$, and MgO, were studied by DRIFTS, XRD, and vapor sorption analyzer. It found that the hydrophilic property of all these particles was enhanced by reaction with acetic acid. Moreover, the results also showed that reaction mechanisms are dependent on the mineralogy of particles as well as the reaction RH conditions. For α-Al_2O_3, the reaction is limited to surface with the formation of surface coordinated acetate under both dry and humid conditions. For MgO, the bulk of particle is involved in reaction and $Mg(CH_3COO)_2$ is formed under both dry and humid conditions, although it exhibits a saturation effect under dry condition. In the case of $CaCO_3$, acetic acid uptake is limited to surface under dry condition while it leads to the decomposition of the bulk of $CaCO_3$ under humid condition. While coordinated surface acetate species increased the water adsorption capacity slightly, the formation of bulk acetate promoted the water absorption capacity greatly. This study is helpful for understanding the environmental and climate impacts of mineral dust.

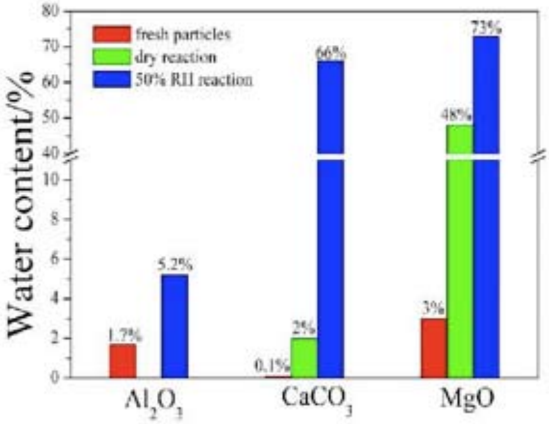

Fig. 1 Water content of Al_2O_3, $CaCO_3$, and MgO at 90% RH with different state: fresh particles, acetic acid reacted under dry condition and at 50%RH.

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RC15

INTERACTIONS BETWEEN EU(III), PHENOLIC ACIDS AND ALUMINA NANOPARTICLES

Moreau P.[1]*, Colette-Maatouk S.[1], Reiller P. E.[1], Gibert-Brunet E.[2], Gareil P.[3]

[1] Commissariat à l'Energie Atomique et aux Energies Alternatives, DEN/DANS/DPC/SEARS/LANIE, Gif-sur-Yvette, France
[2]Direction Générale de l'Armement, Bagneux, France
[3]Chimie Paristech, Laboratory of Physicochemistry of Electrolytes, Colloides and Analytical Sciences, Paris, France

pauline.moreau@cea.fr

Natural colloid-borne transport of metal ions in ground water is known to occur. The implications of this kind of transport are especially important in the context of radionuclide migration in subsurface water to evaluate risks of pollutants migration in contaminated soils [1,2]. Furthermore, dissolved organic matter plays a crucial role on metal ions transport. In particular, phenolic acids, resulting from lignin degradation, may be involved in the process of metal ion adsorption onto mineral nanoparticles, as it is the case for aliphatic acids [3]. Our aim is to investigate the sorption of Eu(III) (rare earth and analogue of trivalent actinides) onto Al_2O_3 nanoparticles in the presence of a hydroxybenzoic acid series (4-hydroxybenzoic, 3,4-dihydroxybenzoic, and 3,4,5-trihydroxybenzoic acids).

First, the binary systems were characterized. Eu(III) was shown to have a high sorption capacity on our Al_2O_3 sample, as already described elsewhere [4,5]. Combining sorption data analysis with time-resolved luminescence spectroscopy (TRLS) for Eu(III), at least 2 sorption sites of different energies were evidenced, as in Rabung et al. [5]. Complexation constants between Eu(III) and acids were determined using TRLS. It appears that the complexation constant increases from log10K° = 2.1 to 5.3 with the number of phenoxy groups on the benzoic ring. As expected, the sorption isotherms of the Al_2O_3-phenolic acid binary systems show different sorption capacities that cannot be explained by the hydrophobicity of the acids Indeed 4-hydroxybenzoic acid, which is the most hydrophobic compound of the series, has the lowest sorption capacity on Al_2O_3. These results are consistent with published data, demonstrating that increasing the number of phenoxy groups on the benzoic ring of analogue compounds increases sorption on alumina [6]. Besides, the sorption isotherm of 3,4,5 trihydroxybenzoic acid at pH 5 can only be fitted using sequential Langmuir isotherms, which evidences different sorption sites for this acid on Al_2O_3.

The same strategy was applied to study the ternary systems. Sorption isotherms were obtained as well as the TRLS spectra which permit to discuss the pertinency of mixed-surface complexes that involves Eu(III), hydroxybenzoic acids and aluminol sites.

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RC16

SORPTION OF ORGANICS CONTAMINANT BY CLAYEY SOIL CONTAMINATED WITH HEAVY METALS

Budianta Wawan*

Dept. Geological Engineering, Universitas Gadjah Mada, Indonesia

wbudianta@ugm.ac.id

The aim of this work was to investigate the effects of sorption of polycyclic aromatic hydrocarbons (PAHs) by Yogyakarta clayey soil contaminated with heavy metal cocontaminants. This work was done considering that beside heavy metals, organics contaminant such as polycyclic aromatic hydrocarbons (PAHs) found in municipal waste. The mechanisms were evaluated, based on the observed of the values of Kd for PAHs sorption by our clayey soil sample. Laboratory batch studies were conducted to investigated and evaluate the sorption capacity of Napthalene, as a representative of PAHs was used in this experiment in our sample with Pb co-contaminant. Based on our observations in this simple laboratory work, the enhancement of napthalene sorption would be more significant by the sample with higher concentrations of Pb. However, this preliminary result needs to be evaluated deeper in future such as the effect of organic matter in the clayey soil sample, the impacts of ageing process of Pb in our sample also need to be investigated. This preliminary result would be helpful to the further assessment and remediation of soils contaminated with combination contaminants of PAHs and heavy metals.

RC17

COMPETITION BETWEEN GLYPHOSATE AND PHOSPHATE FOR THE SURFACE OF GOETHITE. ADSORPTION AND LIGAND EXCHANGE

Avena M.[1]*, Waiman C.[1], Zanini G.[1], Regazzoni A[2]

[1] INQUISUR-CONICET. Departamento de Química, Universidad Nacional del Sur, Bahía Blanca, ARGENTINA.
[2] CONEA-Comisión Nacional de Energía Atómica, Centro Atómico Constituyentes,
Buenos Aires, and Instituto de Tecnología Jorge Sabato, Universidad Nacional de
General San Martín, San Martín, Argentina.

mavena@uns.edu.ar

Glyphosate is a broad spectrum herbicide used in agriculture for the control of many different weeds. As a consequence of its widespread use, this herbicide has been found in surface waters, streams and other sites. The mobility and availability of glyphosate in the environment is strongly influenced by adsorption-desorption processes on minerals, particularly ferric oxides and hydrous ferric oxides. Glyphosate mainly adsorbs on these minerals by a ligand exchange process, resulting in the formation of inner-sphere surface complexes where the phosphonic group of the molecule binds Fe atoms at the surface displacing coordinated water molecules and/or hydroxyl ions. In natural environments, glyphosate adsorption on mineral surfaces is affected by pH, ionic strength and the presence of other substances such as other pesticides, ions, organic matter, fertilizers, surfactants, etc. Phosphate ions, for example, have a strong effect on glyphosate adsorption. Phosphate is a macronutrient for plants, and it is frequently applied to soils as a fertilizer. As it occurs with glyphosate, phosphate adsorbs on Fe and other mineral surfaces by forming inner-sphere complexes, and could compete with glyphosate for the same adsorption sites.

In this work, the competition between glyphosate and phosphate for the surface of goethite is presented. More specifically, the desorption kinetics of glyphosate as induced by the presence of phosphate is discussed. The studies were performed by attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR), by first adsorbing glyphosate at different surface coverages and then adding phosphate to induce desorption. Data were complemented with individual glyphosate and phosphate adsorption isotherms and electrophoretic mobility measurements. The results show that both, glyphosate and phosphate adsorb strongly on goethite. ATR-FTIR is able to explore the goethite-solution interface at the molecular level, allowing the in-situ identification of the formed inner-sphere complexes. In desorption experiments, it was also possible to simultaneously quantify as a function of time the desorption of glyphosate complexes and the adsorption of phosphate complexes. When glyphosate is initially adsorbed at low surface coverages, added phosphate adsorbs mainly on free surface sites displacing a small amount of gyphosate. When the herbicide is initially adsorbed at high surface coverages, phosphate addition displaces significantly glyphosate from adsorption sites. Under these conditions, a phosphate-glyphosate ligand exchange can be observed. In view of the similarities in the structures of phosphate and the phosphonic moiety of glyphosate, it can be concluded that they are strong competitors for the goethite surface. Phosphate may thus play an important role in determining the bioavailability and leaching potential of glyphosate.

CONICET, CONEA, ANPCYT, UNS and UNSAM are acknowledged.

RC18

CO-ADSORPTION OF ENROFLOXACIN AND COPPER(II) ON A CHALKY SOIL

Graouer-Bacart M., Sayen S.,* Guillon E.

Institut de Chimie Moléculaire de Reims (ICMR), UMR CNRS 7312, Université de Reims
Champagne-Ardenne, Faculté des Sciences, B.P. 1039, F-51687 Reims Cedex 2, France

stephanie.sayen@univ-reims.fr

This work is part of a multidisciplinary research program whose main objective is to provide a better knowledge of the fate and impact of emerging pollutants coming from the health sector in environment, more particularly at water/soil and water/sediment interfaces. The issues concern not only the protection of the environment and public health, but also the improvement of water treatment technologies.

Among emerging organic pollutants, antibiotics are widely used in human and animal medicine, and reach the environment through two main pathways. On the one hand, since current treatments are not well adapted to these pollutants, they can be found in effluents from wastewater treatment plants. On the other hand, they can reach soils via animal dejections and sewage sludge spreading, and reach afterwards the groundwaters by infiltration. During their transfer through soils, sorption processes play a key role in their mobility.

In this context, the aim of our work is to study the adsorption of the antibiotic enrofloxacin on a chalky soil. The influence of various parameters such as contact time, pH, concentration and ionic strength is presented. The adsorption studies are also conducted in presence of copper(II), an ubiquitous inorganic pollutant in the environment. Indeed, it is known that metallic cations can modify the sorption properties of organic pollutants. Moreover, we have previously characterized in our laboratory a copper-enrofloxacin complex [1]. Finally, a molecular scale study (XANES and EXAFS) will be presented in order to confirm the role of copper in enrofloxacin retention.

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HIGHLY EFFICIENT REMOVAL OF METHYL MERCAPTAN AND CARBONYL SULFIDE TRACES USING ADSORPTION AND CATALYSIS ON ZEOLITES AND LAYERED DOUBLE HYDROXIDES

Trens Philippe[1]*, Ryzhikov Andrey[1], Hulea Vasile[1], Tichit Didier[1], Leroi Catherine[2], Anglerot Didier[2], Coq Bernard[1]

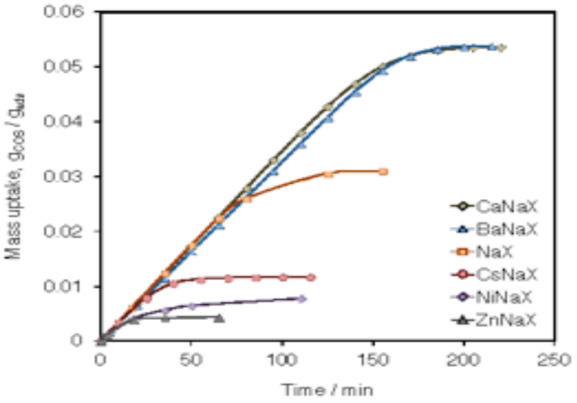
[1]ICGM, UMR 5253 CNRS/ ENSCM / UM2 / UM1, "Matériaux Avancés pour la Catalyse et la Santé", 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France.
[2]TOTAL SA, Pôle Recherche et Développement Mont/Lacq, BP 47 – 64170, Lacq, France.

philippe.trens@enscm.fr

Natural gas always contains contaminants or other unacceptable substances including hydrogen sulfide, carbonyl sulfide or mercaptans [1]. Conditioning natural gas generally requires the removal of these contaminants, which comprises several main operations among which deacidizing. The deacidized gas usually contains 2% CO_2, 4 ppm H_2S and 20-50 ppm total sulfur (mercaptans and COS). In view of both increasingly stringent environmental regulations, deeper desulfurization becomes in high demand. On that account, we present new results describing the highly efficient elimination of CH_3SH and COS traces in CH_4, in relation with adsorption and heterogeneous catalytic processes using original adsorbents and catalysts.

Some results

On the other hand, the affinity of COS was found lower in comparison with CH_3SH. Generally, for a given zeolite structure, the global adsorption of CH_3SH for metal-exchanged zeolites was found to increase with the basicity and the valence of the cation. The catalytic hydrolysis of COS was performed on the same materials to compare the conversion of COS related to the affinity of COS species for the different materials. We found that there are considerable differences of activity among the catalysts, indicating that the nature of the cations plays a major role. LDHs with different composition, as well as mixed oxides, derived from LDHs by calcination, were also screened for their ability to catalyze the COS hydrolysis. Mixed oxides proved highly active catalyst in COS hydrolysis.



Conclusions

The basicity of the catalysts was found to rule the hydrolysis. The LDH-based materials are far more active catalysts than the Me-zeolites. The CO_3^{2-}- containing mixed oxides exhibited outstanding catalytic activity for COS hydrolysis performed at temperatures lower than 100°C.

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COMPARATIVE REDUCTION KINETICS OF BOTH ORGANIC AND INORGANIC POLLUTANTS BY CHEMICALLY SYNTHESIZED AND BIOMINERALIZED FEII-FEIII GREEN RUSTS

Remy P.-P.*[1], Hazotte A.[1], Sergent A.-S.[1], Estrade N.[2], Hanna K.[1,3], Jorand F.P.A.[1]

[1]Université de Lorraine LCPME UMR 7564 CNRS–UL, 405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, France.
[2]CNRS, CRPG UPR 2300, 15, rue Notre-Dame des Pauvres 54501 Vandoeuvre-les-Nancy, France.
[3]Present address: Sciences Chimiques de Rennes UMR CNRS 6226 (ENSR), Equipe CIP, Av. du Gal Leclerc, 35708 Rennes, France.

paul-philippe.remy@lcpme.cnrs-nancy.fr

Green rusts (GR) are mixed ferrous–ferric hydroxides that have layered structures consisting of alternating positively charged hydroxide layers and hydrated anion layers. These compounds can be obtained by chemical co-precipitation of FeII and FeIII species or from bioreduction of ferric oxides by iron reducing bacteria. They exhibit high reactivity with both organic and inorganic pollutants. While numerous works were mainly focused on chemically synthesized GR, no study, to our knowledge, has reported the reactivity of biogenic GR. The biogenic GR are known to be more stable over time (several years in aqueous phase) than those chemically synthesized probably due to the presence of exo-polymeric substances or bacterial cells surrounding the crystals. This work is devoted to compare the reactivity of chemically and biologically synthesized GRs against an organic pollutant, the methyl red (MR) and an inorganic one, the cationic mercury (HgII). Reductive transformation of MR was monitored by spectrophotometric method and cationic mercury by ICPMS. Results show that both abiotic and biotic carbonated GR can reduce HgII (Fig. 1) and MR. The biomineralized carbonated GR(CO_3^{2-}) appeared to be equivalently reactive than the chemically synthesized counterpart as well as the sulfated GR(SO_4^{2-}) in spite of its higher stability. The effect of other stabilizing agents such as phosphate on the GR(CO_3^{2-}) reactivity was also tested.

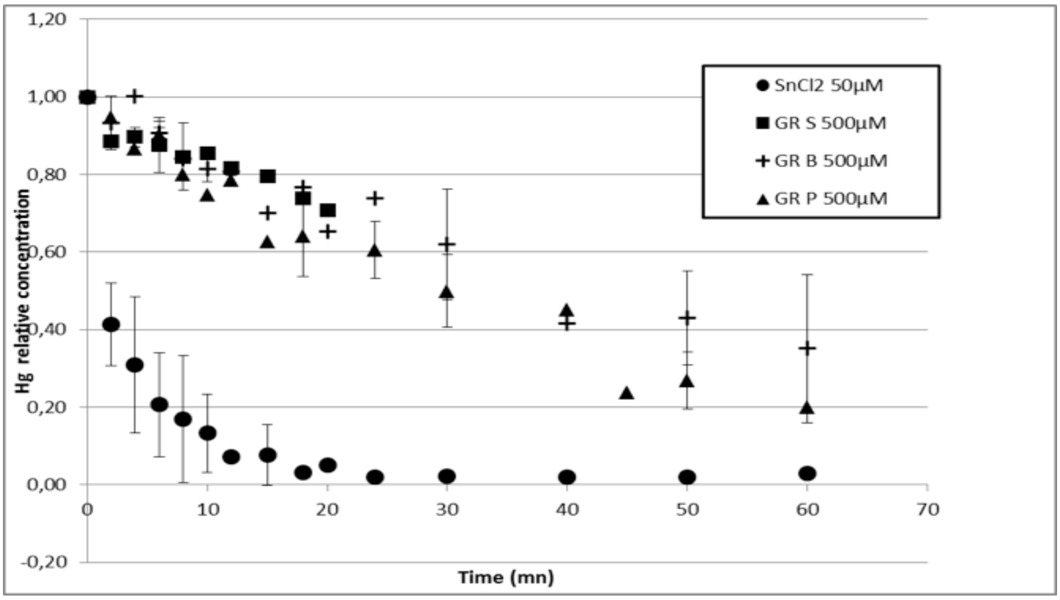

Figure 1 : Evolution of HgII relative concentration during the reaction with sulfated green rust (GR S), carbonated biogenic green rust (GR B), carbonated green rust stabilized by phosphates (GR P) and $SnCl_2$.

SELECTIVITY AND REACTIVITY OF HYDROXYCARBONATED GREEN RUST DURING NITRATE REDUCTION: EFFECTS OF PH, PHOSPHATE AND TOTAL IRON CONCENTRATION

Etique M.,* Zegeye A., Barthélémy K., Grégoire B., Carteret C., Ruby C.

Laboratoire de Chimie Physique et Microbiologie pour l'Environnement. LCPME, UMR 7564,
Université de Lorraine, CNRS. 405 rue de Vandoeuvre, F-54600 Villers-lès-Nancy, France.

marjorie.etique@lcpme.cnrs-nancy.fr

The high standards for drinking water quality set by the European Union and the World Health Organization have led to development of technologies based on iron compounds for denitrification processes of wastewater and groundwater treatments. For instance, the layered FeII-FeIII double hydroxides, known as green rusts, can reduce nitrate to ammonium with their subsequent transformation to magnetite $Fe^{II}Fe^{III}_2O_4$ [1]. In this present work, the ability of the hydroxycarbonated green rust ($GR1(CO_3^{2-})$) to reduce nitrate by restricting ammonium formation was investigated.

$$4\ Fe^{II}{}_4Fe^{III}{}_2(OH)^{12}CO_3(s) + NO_3^- + 6OH^- \leftrightarrow 8\ Fe_3O_{4(s)} + NH_4^+ + 4\ CO_3^{2-} + 25\ H_2O$$

To fulfill this goal, ammonium selectivity (SNH_4^+) (i) and reactivity (kobs) of the reaction were analyzed through a full factorial design. Four parameters known to affect strongly nitrate reduction were studied: the initial nitrate concentration (0.81 – 3.23 mM), the amount of total iron constituting the carbonated green rust (62.5 – 250 mM), the phosphate concentration stabilizing the $GR1(CO_3^{2-})$ (0 – 1 mM), and the initial pH of the reaction (7.5 – 10.5). The results of the full factorial design showed that the lowest selectivity values toward NH_4^+ are obtained with a low total iron concentration and a high phosphate concentration. On the contrary, a high kobs is affected by a basic solution (pH = 10.5), a great amount of total iron concentration, and a low concentration of phosphate.

For the first time, only 35% of reduced NO_3^- species were converted into NH_4^+ species – which is the lowest value ever reported – with a rate of 8 10^{-7} s^{-1} (Figure 1).

(i) SNH_4^+ corresponds to the ratio of produced ammonium to reduced nitrate

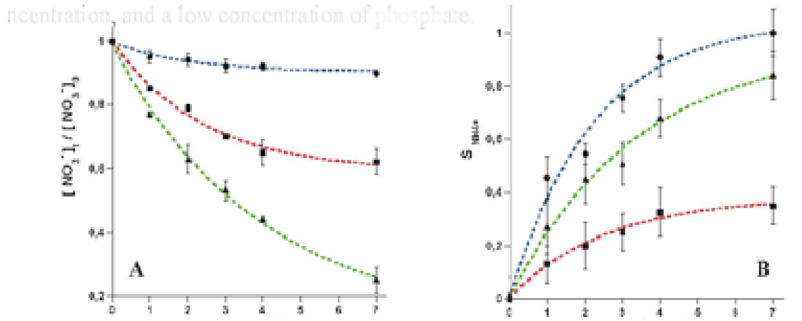

Figure 1. Rate of nitrate consumption (A) and ammonium selectivity (B) with accompanying first-order fits
round: $[NO_3^-]_i = 0.81$ mM; $[Fe_{tot}] = 250$ mM; $[PO_4^{3-}] = 1$ mM; $pH_i = 7.5$
square: $[NO_3^-]_i = 0.81$ mM; $[Fe_{tot}] = 250$ mM; $[PO_4^{3-}] = 0$ mM; $pH_i = 7.5$
triangle: $[NO_3^-]_i = 3.23$ mM; $[Fe_{tot}] = 62.5$ mM; $[PO_4^{3-}] = 0$ mM; $pH_i = 10.5$

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PC1

COMPARATIVE STUDY OF THE PROMOTIONAL EFFECT OF SECOND METAL (V, MO, W OR CE) FOR THE LOW TEMPERATURE SCR OF NO_X WITH NH_3 OVER DERIVED SOL GEL MODIFIED TIO_2

Arfaoui J.[1]*, Ghorbel A.[1], Pettito C.[2], Delahay G.[2]

[1]Laboratoire de Chimie des Matériaux et Catalyse, Faculté des Sciences de Tunis, Département de
Chimie, Campus Universitaire 2092, Tunis El Manar, Tunisia.
[2]Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier, 34296, France

jihenar@yahoo.fr

Aerogels mixed oxides catalysts, labelled as V_2O_5-TiO_2, MoO_3-TiO_2, CeO_2-TiO_2 and, WO_3-TiO_2 were synthesized by supporting transition or rare earth metal (V, Mo, W or Ce) on the TiO_2 anatase surface using the one step sol gel method. All the catalysts were characterized by means of XRD, N_2-Physisorption, H_2-TPR and NH_3-TPD techniques and then tested in the selective catalytic reduction of nitrogen oxide (SCR-NO) by NH_3 in 150- 500 °C temperature range, using a molar ratio $NH_3/NO = 1$ and oxygen rich atmosphere. The result showed that the incorporation of the second metal (V, Mo, W or Ce) does not affect the cristalline anatase phase of the TiO_2 support but decreases both its surface area and total acidity. On the other hand, it was shown that the the presence of V, Mo or Ce species enhanced significantly the reductibility of the binary V_2O_5-TiO_2, MoO_3-TiO_2 and CeO_2-TiO_2 compared to the TiO_2 support or the WO_3-TiO_2 catalyst. In the SCR-NO by NH_3, it was found that the catalysts containing V, Mo or Ce species exhibit more higher NO conversion at low temperature compared to the catalyst containing W. The high catalytic performance of V_2O_5- TiO_2, MoO_3-TiO_2 and CeO_2-TiO_2 catalyst, at low temperature, is essentielly attributed to the redox sites creates by vanadium, molybdenium or cerium species on the TiO_2 surface. Among all the catalysts tested it was revealed that CeO_2-TiO_2 is the more active at low temperature (250-300°C) suggesting the potentiel role of redox sites created by cerium for low temperature $DeNO_x$ process.

Keywords: TiO_2, V_2O_5, MoO_3, CeO_2, WO_3, Low temperature $DeNO_x$ process.

PC2

ACID AND ALKALI EFFECT ON SURFACE PROPERTIES OF SOILS AND THEIR MINERAL CONSTITUENTS

Cieśla J.*, Józefaciuk G., Bieganowski A., Łukowska M.

Institute of Agrophysic PAS, Doświadczalna 4, 20-290 Lublin, Poland

j.ciesla@ipan.lublin.pl

Physicochemical properties of the surfaces of soil particles are strongly influenced by various environmental and anthropogenic factors, which can lead to soil degradation. Acidification and alkalization are the most important soil degradation processes. The problem of this work is to characterize their effects on changes of soil surface properties. The solid phase of soil is very complicated system due to its complex chemical composition, mineralogy, organic matter content and quality, varying particle size distribution. During acidification of clay poor soils a decrease of the variable charge is observed, whereas for clay rich soils this charge increases. The alkalization generally results in decrease of the variable charge [1]. The surface area decreases for both the acidified and alkalized clay poor soils. However, for the soils which are rich in clay fraction, as well as for pure minerals, the increase of surface area occurs. The average adsorption energy on solid phase decreases in acidic as well as alkaline media what reflects the lowering of water binding forces. An extreme decrease of pH leads to the decrease of fractal dimension of clay fraction what suggests that the particles surface become smoother [2].

Response of the soil surface properties on the alkalization and acidification is mainly connected with:

- dissolution of Al and Fe oxides of large surface area in both alkaline and acidic environment
- formation of amorphous silica and destruction of mineral lattice (in acidic media),
- depletion of mineral silica sheets in alkaline media
- dissolution of the organic matter of high charge and surface area.

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PC3

EVALUATION OF PHOSPHOROUS ADSORPTION AND DESORPTION CAPACITY OF EPISAMMIC BIOFILMS DEVELOPED ON STREAMBED SEDIMENTS

Prieto D.M.[1]*, Devesa-Rey R.[2], Díaz-Fierros F.[1], Barral M.T.[1]

[1]Dpt. Soil Science and Agricultural Chemistry. Fac. Farmacia. Campus Vida. 15782. Santiago de Compostela - Spain
[2]Dpt. Chemical Engineering. Escuela de Ingeniería Industrial – Sede Campus. As Lagoas, Marcosende, 36310.
Vigo - Spain.

diego.martina@usc.es

Phosphorous (P) is one of the most common contaminants in rivers due to its potential to cause eutrophication. The development of episammic biofilms on the riverbed sediments can improve the P adsorption capacity, involving the removal of this pollutant in the overlying water, and at the same time can reduce the P desorption process in order to retain this possible contaminant. The main aim of this study was the assessment of the phosphorous adsorption and desorption behaviour of episammic biofilms as a potential useful tool to the bioremediation of situations with problematic P concentrations. An entire biofilm growth was carried out during 15 days over 8 g of riverbed sediment, replacing the overlying river water each 5 days and introducing 0.5 mL of inoculum in order to stimulate the growth. Once the biofilm was developed, the overlying water was removed. In order to determine the adsorption isotherm, 60 mL of different initial P (P_0) concentrations (0, 0.25, 0.5, 1, 2 and 3 mg/L) prepared in 0.01 M $CaCl_2$ solutions were added to the systems. All the samples were prepared by triplicate and the equilibrium was reached in 24 h. After that 55 mL of the overlying water were removed and 55 mL of 0.01 M $CaCl_2$ solutions were added in order to obtain the desorption isotherm. Again the equilibrium was reached in 24 h and 55 mL of the overlying water were removed. Phosphorus equilibrium (P_e) concentration of the samples was determined by means of an acid digestion with H_2SO_4 followed by colorimetric determination with ammonium molybdate [1]. Adsorbed phosphorous (P_{ads}) concentrations were obtained by the difference between P_0 and P_e. Freundlich and Langmuir models isotherms were used to fit satisfactory the adsorption isotherm with values of R2 of 0.92 and 0.95, respectively. Therefore Lagmuir isotherm is the most suitable model to adjust experimental data. The maximum adsorption capacity of the sediment given by Langmuir model was 0.019 mg/g. The percentage of P_{ads} with respect to P_0 was of 80.24 ± 8.23 %. An exponential growth model to describe the amount of P desorbed (P_{des}) was applied in this study [2], determining a value of R^2 of 0.92. The values of parameters a and b (desorption potential and desorption rate, respectively) were of 1.34 10-4 mg g^{-1} and 1.48 102 g mg^{-1}, respectively. The percentage of P_{des} with respect to Pads was of 7.49 ± 1.63 % so hence the percentage of retained P with respect to P_{ads} was of 92.51 ± 1.63 %. In conclusion the biofilm obtained by this study adsorbed an important part of the phosphorous of the overlying water and desorbed a small quantity of it which shows the great role that it could play in bioremediation and in decontamination processes.

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PC4

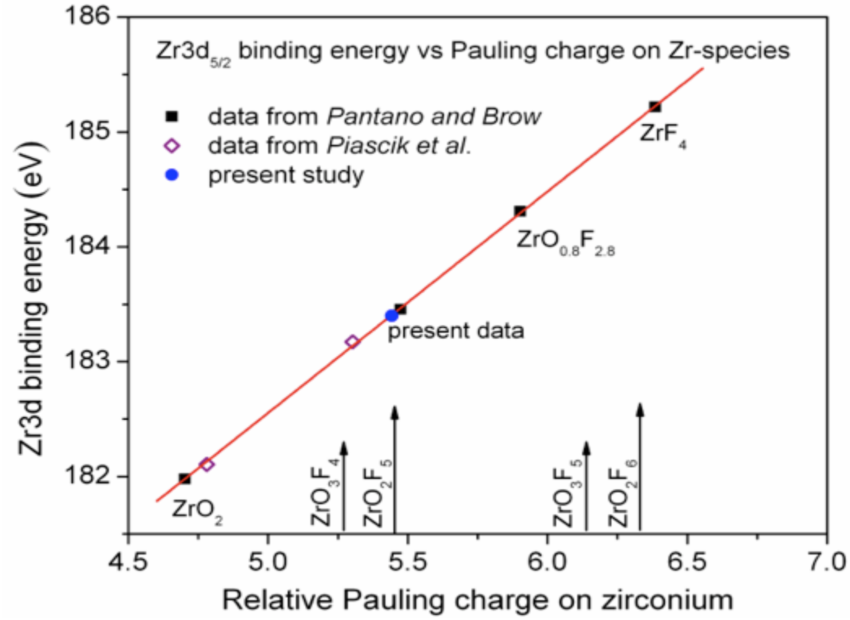
REMEDIATING FLUORIDE FROM WATER USING HYDROUS ZIRCONIUM OXIDE

Dou X.M.[1]*, Mohan D.[2], Pittman, Jr. C.U.[3], Yang S.[1]

[1] College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China;
[2] School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India
[3] Department of chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States;

douxiaomin@bjfu.edu.cn

The defluoridation performance and adsorption mechanism of a high capacity hydrous zirconium oxide adsorbent were investigated. Maximum adsorption capacities of 124 and 68 mg-F^-/g-adsorbent were obtained in batch studies at pH 4 and 7. Capacity increased continuously with decreasing pH. Hydrous ZrO_2 is superior to most Zr-containing adsorbents. Surface titration and Zeta potential measurements defined this adsorbent's surface charging behavior and the electrostatic interactions between fluoride and surface charge. Inner-sphere complexes formed after adsorption. The pH_{zpc} was 6.7. Raman and FTIR observations provided direct evidence for the exchange reaction between surface hydroxyl groups with fluoride. XPS and 19F NMR analyses indicated that seven-coordinate polyhedral zirconium oxyfluoride species, ZrO_2F_5 (Fig. 1),formed on the adsorbent's surface by exchange reactions between surface hydroxyl groups with fluoride, through either associative or dissociative pathways of fluoride uptake. Finally, surface reactions were suggested based on all the experimental results.



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PC5

ELECTROLYTE INTERFACE : CHALLENGING MACROSCOPIC APPROACHES FOR ION SPECIFICITY ISSUES

Duval J.F.L.[1]*, Bera S.[2,3], Michot L.J.[1,] Daillant J.[2], Belloni L.[2], Konovalov O.[4], Pontoni D.[4]

[1]LEM, Université de Lorraine, CNRS UMR 7569, 15 avenue du Charmois, B.P. 40, 54501 Vandoeuvre-lès-Nancy, France.
[2] Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, UMR 3299 CEA/CNRS, CEA Saclay, 91191-Gif-sur-Yvette Cedex, France.
[3] Department of Physics, Northern Illinois University, 202 LaTourette Hall, Dekalb, IL 60115, USA (current address).
[4] European Synchrotron Radiation Facility. 6 rue Horowitz, B.P. 220 F-38043 Grenoble Cedex, France.

jerome.duval@univ-lorraine.fr

For more than 60 years, the liquid Hg/electrolyte interface has been used as a model system to test electrical double layer theories. In particular, macroscopic interfacial tension of externally polarized Hg/electrolyte interface (electrocapillary curves) were extensively collated with the well-known Gouy-Chapman-Stern (GCS) model [1], and were recently confronted to Anisotropic HyperNetted Chain (AHNC) simulations [2]. Comforting or not the fundaments of these theories for deciphering ion spatial distributions at charged interfaces and for interpreting ion-specific phenomena, still critically requires molecular-scale data on interfacial structure and composition. In this study, we use for the first time X-ray reflectivity to achieve an Angstrom-resolved description of the interface between polarized Hg and aqueous solutions containing 1M LiCl, 1M LiBr or 2M $MgSO_4$ [3]. The analysis reveals a number of key features so far incorrectly ignored in the traditional thermodynamic derivation of electrocapillary data, and in their interpretative framework based on standard GCS model or molecular electrostatic model that includes ion-ion correlations [2]. Our molecular-scale reflectivity measurements dismiss the long-standing approximation that assimilates Hg surface to a smooth, perfect chemically-inert conductor with uniformly smeared-out surface charge density. Instead, Hg interfacial roughness is shown to depend on ion nature and applied potential according to capillary wave theory ('Hg layering') and an 'incomplete Hg layer' containing Hg atoms entering the liquid phase, substantially contributes to the overall distribution of charged species at the polarized interface. Potential- and ion-dependent electronic properties of polarized Hg surface are incorrectly discarded in available models for tackling ion specificity issues at Hg surface.

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PC6

ADSORPTION OF CU(II) BY AMINOPROPYL-FUNCTIONALIZED MESOPOROUS δ-MNO$_2$ FROM AQUEOUS SOLUTION

Zhang Hao[1, 2], Wang Hongjie[1,] *, Xu Meng[1], Lei Di[1], Qu Dan[1], Zhai Yujia[1]

[1] College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China
[2] College of Environmental Science and Engineering, Heibei University of Science and Technology, Shijiazhuang 050018, P.R. China

whj_99@hotmail.com

A novel adsorbent, named aminopropyl-functionalized mesoporous δ-MnO_2 (NH_2-MnO_2), was synthesized by bounding 3-aminopropyltriethoxysilane (APTMS) onto δ-MnO_2 surface. The amount of APTMS grafted on δ-MnO_2 was found to be 110 mg/g by thermogravimetric analysis (TGA). The specific surface area, pore volume and BJH pore diameter of the NH_2-MnO_2 was 79.31 m2/g, 0.19 cm^3/ g and 9.5 nm. X-ray powder diffraction (XRD) indicated the characterization of NH_2-MnO_2 was accordance with the synthesized δ-MnO_2 before and after Cu(II) adsorption. Transmission electron microscopy (TEM) images showed the mesoporous characterization of NH_2-MnO_2. Scanning electron microscopy (SEM) images revealed that the amorphous nano particles formed aggregates. The fourier-transform infrared spectroscopy (FTIR) results verified the formation of the band of Mn-O-Si and the grafting of APTMS onto NH_2-MnO_2. The adsorption isotherm at 298 K could be well described by Langmuir isotherm equation. The maximum adsorption capability of NH_2-MnO_2 and the un-functionized δ-MnO_2 for Cu(II) at pH 4.0 was 94.93 mg/g and 78.24 mg/g, respectively. The competing adsorption of Cu(II) and Pb(II) onto the NH_2-MnO_2 and the un-functionized δ-MnO_2 was also investigated in binary component system. The results showed that the molar ratio of the adsorbed Cu(II) and Pb(II) by un-functionized δ-MnO_2 and NH_2-MnO_2 increased from 0.12 to 0.69, which indicated the enhancement of the selectivity of NH_2-MnO_2 for Cu(II).

Keywords: Adsorption, Heavy metal, Mesoporous material, Manganese dioxide, Organic silane

PC7

INFLUENCE OF SOLUTION PARAMETERS ON EUROPIUM(III), α-AL$_2$O$_3$ AND HUMIC ACID INTERACTIONS

Janot N.[1,2]*, Reiller P.E.[1], Benedetti M.F.[2]

[1] Commissariat à l'Energie Atomique et aux énergies alternatives, CE Saclay, CEA, DEN, DANS, DPC, SECR, Laboratoire de Spéciation des Radionucléides et des Molécules, Bâtiment 391 PC 33, F-91191 Gif-sur-Yvette Cedex, France.
[2] Université Paris Diderot, Sorbonne Paris Cité, IPGP, UMR CNRS 7154, F-75205 Paris, Cedex 13, France.
Present address: Stanford Synchrotron Radiation Lightsource, 2575 Sand Hill Rd, Menlo Park, CA 94025, United States.

njanot@slac.stanford.edu

Speciation of Eu(III) in the presence of purified Aldrich humic acid (PAHA) and/or aluminum oxide α-Al$_2$O$_3$ has been studied by batch experiments and timeresolved luminescence spectroscopy at different pH, ionic strengths and PAHA concentrations. Macroscopic and spectroscopic data (sorption, spectra, and decay times analyses) are compared between the ternary system, i.e., Eu(III)/PAHA/ α-Al$_2$O$_3$, and the corresponding binary systems.

As expected, results show a weak influence of ionic strength on Eu(III) adsorption onto α-Al$_2$O$_3$. However, in the binary Eu(III)/PAHA system, it is evidenced that variations of electrolyte concentration, which modify PAHA conformation, influence the symmetry of the humic-bound Eu(III) at high pH. In the ternary system, adsorption of both Eu(III) and PAHA onto the surface decreases with ionic strength. At 0.01 mol/L NaClO$_4$, Eu(III) luminescence decay is much faster than at 0.1 mol/L NaClO$_4$. This is most likely due to the lower surface concentration of PAHA at lower ionic strength, leading to a lesser constrained environment for Eu(III) ions. At high pH, luminescence spectra are different at the two ionic strengths studied.

Concerning the influence of PAHA concentration, spectroscopic results show that in the binary Eu(III)/ PAHA system a complete complexation of 1 µmol/L Eu(III) is reached for 16 mg/L PAHA at pH 4, and for lower PAHA concentrations at higher pH. At same PAHA concentration, there is no difference in asymmetry ratios between the binary Eu(III)/PAHA system and the ternary system between pH 4 and 7.7. This means that the presence of mineral surface has almost no influence on Eu(III) environment symmetry below pH 8. Hence, the occurrence of europium-bridged humic surface complexes is not likely. In the ternary system, at different pH, luminescence decay times of Eu(III) increase with PAHA concentration. They are much higher in the ternary system than in the binary Eu(III)/PAHA system, which would mean that Eu(III) environment in PAHA-bound molecules is more constrained, as previously seen [1]. Macroscopic results show that the influence of PAHA on Eu(III) sorption onto α-Al$_2$O$_3$ depends on pH: at low pH, Eu(III) retention is always higher in the ternary system, whereas at higher pH it depends on PAHA concentration.

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COAGULATION AND CHARGING OF LATEX PARTICLES IN THE PRESENCE OF NATURAL CLAY NANOTUBE IMOGOLITE

Kobayashi M.[1]*, Nitanai M.[2], Satta N.[2], Adachi Y.[1]

[1]Faculty of Life and Environmental Sciences, University of Tsukuba, Japan
[2]Faculty of Agriculture, Iwate University, Japan

kobayashi.moto.fp@u.tsukuba.ac.jp

Some coagulants made from natural volcanic ash soils have been developed. Imogolites contained in volcanic ash soil have several unique properties. That is, the imogolites have nano-tubular structure, have positive charge below pH 9, and coagulate beyond pH 6. With these properties, we think imogolites play an important role when coagulants from volcanic ash soils are applied.

To clarify mechanisms of imogolite-induced coagulation and subsequent sedimentation, we have studied the coagulation and charging of three different latex spheres in the presence of purified imogolites taken from natural soil in Kitakami, Iwate, Japan. Coagulation and dispersion were judged by observing latex-imogolite mixed suspensions with the naked eye and by measuring the supernatant absorbance. Charging property was studied by electorophoretic mobility. These experiments were carried out as a function of the ratio of the concentration of imogolites (CI) to that of latex particles (CL) at three different pH.

The experimental results clarified that the mechanism of imogolite-induced coagulation depends on the properties of charging and coagulation of imogolites. That is, when the latex and the imogolite are oppositely charged and the imogolites are dispersed, coagulation occurs (eg, Fig.1a) only around isoelectric point. In this case, charge neutralization gives rise to coagulation. If the latex and the imogolite are oppositely charged and the imogolites are coagulated, coagulation occurs not only around isoelectric point but also at higher CI/CL (eg, Fig.1b). This result indicates that coagulation is due to charge neutralization as well as sweep coagulation, where the latex particles are enmeshed by flocs of imogolites. When the latex and the imogolite are similarly charged and the imogolites are coagulated, coagulation of the mixture occurs at higher CI/CL (eg, Fig.1c) by only the sweep coagulation.

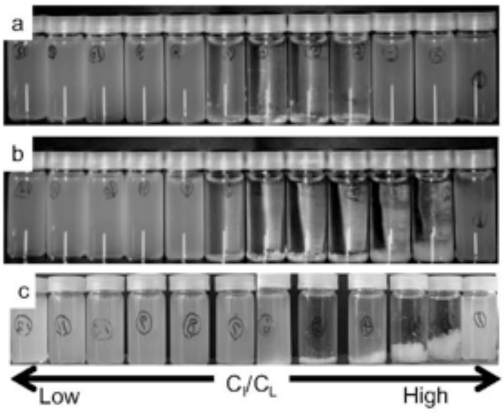

Fig. 1 Aggregation and sedimentation of mixed suspensions of negatively charged latex and imogolites: (a) imogolites are positively charged and dispersed, (b) imogolites are positively charged and coagulated, (c) imogolites are negatively charged and coagulated.

PC9

EFFECTS OF GEOCHEMICAL CONDITIONS ON THE SORPTION OF URANIUM, NEPTUNIUM, AND AMERICIUM BY GRATITE

Lee J. K.*, Baik M. H., Jeong J. T., Choi J. W.

Radioactive Waste Disposal Research Division, Korea Atomic Energy Research Institute,
Daedeokdaero 989-111, Yuseong-Gu, Daejeon 305-353, Rep. of Korea

jklee1@kaeri.re.kr

Sorption experiments were carried out to investigate the effects of geochemical conditions such as redox potential (Eh), pH and constituent minerals on the sorption of uranium, neptunium, and americium sorption by granite. The granite samples were obtained from rock cores (YH 1-1, KP 1-20, KP 1-32) at the KAERI Underground Research Tunnel (KURT) located within the Korea Atomic Energy Research Institute (KAERI) site. Granite mainly consists of quartz, plagioclase, K-feldspar, microcline, muscovite, and minor minerals including chlorite and biotite. The used groundwater was also sampled from a borehole (DB-1) of KURT below -200 m from the surface.

The distribution coefficients (Kd) of uranium were reduced from 44±26 to 27±8 mg/L when the redox potential was decreased from ~-0.3 to ~+0.3 V with a $Na_2S_2O_4$ solution. The effects of the redox potential on neptunium sorption were more significant than those of uranium. When the redox potential of the solution was ~-0.3 V, the Kd values of neptunium were measured as 177.1±74.1 mL/g. As the redox potential increased to +0.3 V, the neptunium sorption was significantly decreased with the Kd values of 14.8±6.9 mL/g. It suggests that the changes in the redox potential of a solution might alter the chemical properties of redox sensitive actinides such as uranium and neptunium, inducing a change in the sorption properties [1, 2]. The effects of pH on the sorption of neptunium and americium were also studied. Experimental results showed that the sorption of neptunium and americium by granite was dependent on the pH.

The sorption of uranium and neptunium onto the different KURT granite samples showed that the Kd values were dependent on the mineralogical composition of granite, especially a minor mineral such as chlorite. Kd values increased in accordance with the contents of chlorite in the KURT granite in the order of YH 1-1, KP 1-20, and KP 1-32. Additional sorption experiments were performed to study the effect of chlorite content on the uranium sorption onto a mixture of chlorite and granite. The results show that the sorption of uranium onto granite is greatly affected by the chlorite content.

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HETEROGENEOUS REACTION OF NO_2 ON TIO$_2$: EFFECT OF CRYSTALLINE PHASE ON SURFACE SPECIES

Liu C., Liu Y. C., Ma Q. X., Ma J. Z., He H.*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

honghe@rcees.ac.cn

NO_2 is a major pollutant in atmosphere and its reactivity is of great importance in atmospheric chemistry [1]. Heterogeneous reactions of NO_2 on mineral dust also attract much attention because they not only influence the concentration of NO_2 but also change the surface properties of particles [2]. Titanium oxide is a major component of mineral dust and anatase is widely used for the representive of TiO_2. There are other crystal forms such as amorphous and rutile, however, little attention has been paid to the effect of crystalline phase on heterogeneous process.

In this study, we used in situ DRIFTS to study the heterogeneous reaction of NO_2 on TiO_2 with different crystal forms including amorphous, anatase, and rutile. It demonstrated that surface species were dependent on the crystalline phase of TiO_2. For amorphous TiO_2, chemical adsorbed HNO_3 was detected during NO_2 reaction. This adsorbed HNO_3 was stable even under dry nitrogen purging. As for anatase, monodentate nitrate was proved to be the dominated species on the surface. However, NO_2 had quite weak reactivity on rutile surface and there was no obvious surface species observed in the DRIFTS spectrum.

Further researches indicated that the formation of surface species were related to OH groups on various crystal forms. Isolated OH groups contributed to the formation of adsorbed HNO_3 on amorphous TiO_2, while H-bounded OH groups were in close relationship with the formation of monodentate nitrate on anatase.

These results imply that crystalline phase has great influence on the surface properties and could influence the formation of surface species. Therefore, the chosen of crystalline phase should be considered in the heterogeneous reaction research.

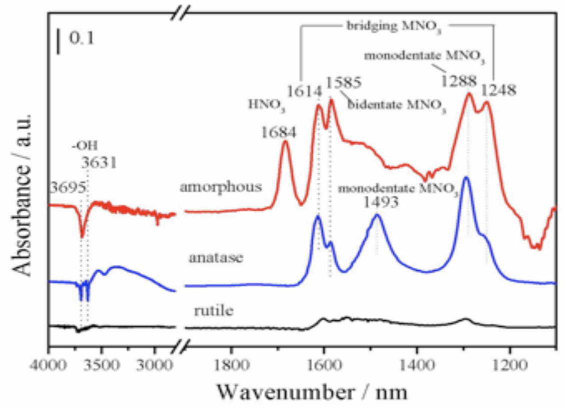

Fig. 1 *In situ* DRIFTS spectra of 200 ppmv NO_2 reaction on TiO_2 samples in a flow of 100 mL/min synthetic air (80%N2, 20% O_2) at 298 K for 3 h.

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BEHAVIOR OF CARBON-14 IN CEMENTITIOUS MATERIALS

Clément L.[1,2]*, Macé N.[2],Pointeau I.[3], Giffaut E.[4], Marmier N.[1]

[1] University of Nice Sophia-Antipolis, ECOMERS, Parc Valrose, 28 avenue Valrose, 06108 Nice Cedex 2, France
[2] CEA - Saclay, Laboratoire de Mesures et de Modélisation de la Migration des Radionucléides (DEN/DANS/DPC/SECR/L3MR), 91191 Gif-sur-Yvette Cedex, France
[3] CEA - Cadarache, Laboratoire de modélisation des Transferts dans l'Environnement, 13108 Saint-Paul-les-Durance Cedex, France
[4] ANDRA, 1/7 rue Jean-Monnet, Parc de la Croix-Blanche, 92298 Chatenay Malabry Cedex, France

Laura.CLEMENT@unice.fr

Carbon 14 is produced in the nuclear fuel cycle following neutron interactions with ^{13}C, ^{14}N, ^{15}N, ^{16}O and ^{17}O, which may be present in the nuclear fuels, like primary and secondary coolant systems of nuclear reactors. In the framework of irradiated graphite waste from the first generation gas-cooled French reactors (UNGG) reprocessing and storage, ^{14}C, as a long-lived betta emitter (T1/2= (5730 ± 30) years) is a radionuclide of interest and its behavior particularly in cementitious system is still poorly known.

^{14}C can occur as inorganic and organic species in cementitious systems. The inorganic form $^{14}CO_3^{2-}$ reflects a low mobility due to high isotope exchange rates with carbonates species present in the concrete materials. However, under the organic form (mainly composed of alkane and short-chain carboxylic acids), ^{14}C is less retained and is expected to be more mobile, particularly for hydrocarbon form.

In the case of a cementitious environment, with a graphite source-term, it is considered that ^{14}C would be released as $^{14}CH_4$ methane, $^{14}CO_2$, ^{14}CO and small carboxylic acid [1].

The aim of this study is to understand the behavior of this radionuclide present as ^{14}C carbonate, ^{14}C-acetate, ^{14}C-formate and ^{14}C-propionate in contact with cementitious materials and to develop an incorporation model of organic and inorganic compounds in cementitious media. This research will firstly focus on the organic fraction, to situate its importance in speciation of carbon element in cementitious environment. It helps to characterize and quantify their interactions with solid phases in static. Sorption studies will be conducted in cementitious materials (isotherms and kinetics of sorption and desorption) in order to investigate the effect of the alkane-chain length onto sorption properties. In parallel, diffusion experiments will be conducted through cement paste materials and in concrete material, in order to determine diffusion parameters of ^{14}C-acetate, ^{14}C-formate and ^{14}C-propionate species.

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PC12

THE ROLE OF THE STARCH MATRIX-KAOLINITE FILLER INTERFACE IN COMPOSITE BIOPOLYMER FILMS

Mbey J. A.[1]*, Hoppe S.[2] and Thomas F.[1]

[1] LEM, UMR 7569 CNRS-Université de Lorraine, B.P. 40, F 54501, Vandoeuvre-Lès-Nancy Cedex
[2] Laboratoire Réactions et Génie des Procédés, UPR CNRS 3349, B.P. 20451, 54001 Nancy Cedex

jean-aime.mbey@univ-lorraine.fr

Starch is a readily available, biodegradable and renewable material that can find use in the production of biodegradable packaging material. However, thermoplastic starch has some drawbacks including poor mechanical properties, water uptake, brittleness and decomposition of the starch matrix [1, 2]. These weaknesses arouse constant interest for properties improvement in thermoplastic starch-based material. In a recent study [3], we introduced a kaolinite clay as filler in cassava starch composite films. The clay was used in its raw and DMSO intercalated forms. Significant changes in mechanical properties, water uptake and heat barrier effects were observed. In the present work we examine these changes in the light of interfacial interactions between starch and
kaolinite.

From dynamical mechanical thermal analysis, a decrease in the glass transition temperature (Tg) of the film is attributed to a plasticizing effect brought by the clay. This plasticizing effect is confirmed by tensile tests through the decrease of the elastic modulus and the increase of the ultimate strength at break. In infra-red spectroscopy, the C-H, O-H and C-OH vibration modes are altered. The water uptake is lowered at 50 % RH and increased at 100 % RH. In all cases, the effects due to the presence of the clay were enhanced when the clay was previously exfoliated by DMSO, since the clay crystallites, split in twofold thinner particles (as indicated by XRD), develop an increased interface with the matrix.

All these observations clearly show that clay-starch interactions are weaker than chainchain interactions in the starch matrix. Weak forces at the clay-starch interface allow sliding of the polymer chains along the interface, which results in increased plasticity. Furthermore, the orientation of the particles strongly depends of the nature of the interfacial forces. In the present case, low repulsive electrostatic forces due to the negative charge of the surface of the clay and the slightly negative (to almost neutral) charge surface of the starch preferentially results in a planar orientation of the clay particles.

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PC13

MODELLING OF SE(IV) SORPTION ON TITANIUM OXIDE COLLOIDS AND EFFECTS OF SORPTION ON COLLOID STABILITY

Benedicto A., Missana T.

CIEMAT, Departamento de Medioambiente, Avenida Complutense 40, 28040 Madrid (Spain)

ana.benedicto@ciemat.es

Natural and anthropogenic colloids in the geosphere can influence the transport of contaminants adsorbed on their surfaces. The presence of TiO_2 colloids in the environment is increasing due to the anthropogenic influx because of their industrial application as white pigments. Due its low solubility and its point of zero charge near to the neutrality, that allows sorption studies in a wide range of environmental conditions, TiO_2 is an ideal model oxide for adsorption studies. Se(IV) is a potentially toxic element at low concentration and its presence in the environment is increased by activities such as mining and combustion of fossil fuels. Se(IV) is susceptible to be transported through the geosphere via TiO_2 or other types of oxide colloids.

This study focuses on two decisive factors concerning colloid-driven migration:

The Se(IV) sorption behaviour on TiO_2 colloids; 2. The stability of TiO_2 colloids before and after the Se(IV)-TiO_2 interaction.

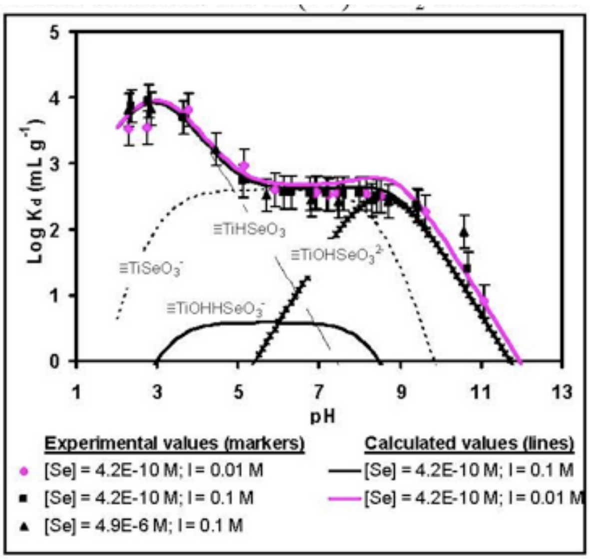

Figure 1. Experimental and modelling of Se(IV) sorption on TiO_2 colloids as a function of pH

1. A surface complexation model was developed to explain Se(IV) adsorption on TiO_2 colloids. Surface complexation constants were obtained by fit a set of experimental batch sorption data obtained in a wide range of pH, ionic strength and Se concentration. The developed model considers one type of sorbing sites on TiO_2 surface and the two Se(IV) anionic specie: SeO_3^{2-} and $HSeO_3^-$. Both inner and outer sphere complexes formation have to be considered to explain sorption experimental data.

2. The size distribution of TiO_2 colloids in suspensions at different pH and ionic strength was determined by Single Particle Counting (SPC) and compared with the size distribution of TiO_2 colloids in suspension after the interaction with Se(IV). Results indicate that the presence of Se adsorbed on the TiO_2 surfaces changes the size distribution of the suspensions at the different studied conditions of pH and ionic strength. The developed sorption model allows a better estimation of the Se colloid-driven migration. In addition, size distribution experiments showed that Se sorption on TiO_2 surfaces modifies the stability of colloids that will influence their movement through the geosphere.

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ADSORPTION PROCESSES IN HETEROGENEOUS ROCK: TOP-DOWN VS BOTTOM UP APPROACH IN MODELLING EXPERIMENTAL DATA.

Missana T., García-Gutiérrez G., Alonso U.

CIEMAT, Department of Environment, Avenida Complutense 40, 28040 Madrid

tiziana.missana@ciemat.es

Crystalline rock presents suitable properties to host a deep geological repository (DGR) of high-level radioactive waste. For this reason, different European countries (Sweden, Finland, Switzerland, Spain, UK) as well as Canada, Japan and USA amongst others analyzed radionuclide (RN) migration in these system for many years.

Adsorption onto rock surface is the main retardation process for solutes migration in flowing paths, thus it is very important to understand the mechanisms controlling it. However, this is not straightforward when highly heterogeneous systems, as crystalline rock, are involved.

These heterogeneous rocks are generally composed of a variety of different minerals therefore retention processes comprise ionic exchange (with constant-charge minerals like micas and clay minerals), surface complexation (with minerals exhibiting pH-dependent surface charge) and (co)precipitation (with carbonates, iron oxides). In the performance assessment of DGRs, sorption is generally handled using the “Kd-approach” and Kd values are experimentally derived, generally from batch experiments with crushed material under site-specific conditions. Mechanistic thermodynamic sorption models are sometimes used to provide support to expert judgment for Kd selection, but their application in crystalline rock is still very limited and a convincing picture of how modelling retention processes is still missing. Sorption in the main constituent mineral affects the indeed sorption, but simply additive models generally do not provide a satisfactory picture of the overall sorption behaviour.

In this work, cesium adsorption onto granites of different origin and onto different minerals composing granite (quartz, feldspar, plagioclase, moscovite and biotite) was analyzed and the modeling of the experimental data was carried out following two different approaches: top-down and bottom-up. The advantages and limitations of both approaches and their applicability to determine reliable Kd values for predicting radionuclide transport in real systems are evaluated.

The research leading to these results has received funding EU Seventh Framework Programme (FP7/2007-2011) under the grant agreement №269658 (CROCK, Crystalline Rock Retention Processes).

PC15

MICRO-SCALE STUDY OF URANIUM RETENTION ON GRANITE

Alonso U.[1]*, Missana T.[1], Patelli A.[2],Ceccato D.[3], García-Gutiérrez M.[1], Rigato V.[3]

[1] CIEMAT, Avda. Complutense 40, 28040 Madrid, Spain
[2] CIVEN, Via delle Industrie 9, 30175 Venezia-Marghera, Italy
[3] INFN-LNL Viale dell' Università 2, 35020 Legnaro-Padova, Italy

ursula.alonso@ciemat.es

Performance assessment studies of deep geological repositories (DGR) for high-level radioactive waste are very sensitive to the selection of radionuclide retention parameters within the repository barriers, especially in highly heterogeneous rock, as granite.

Contaminant retention is generally described by a single distribution coefficient (Kd), obtained on powder material, which may not be sufficient for a heterogeneous material. To provide a sound sorption value, to relate distribution coefficients measured on powder (Kd) and intact rocks (Ka) is still required. Furthermore, to assess the minerals that most contribute to sorption is fundamental. However, very few radionuclide retention data measured on rock surface are available.

This study presents an experimental methodology, applying the ion beam technique micro-Particle Induced X-Ray Emission (mPIXE), to visualize and quantify contaminant distribution coefficients on rock surface at mineral micro-scale.

The retention of uranium onto granite different locations (Spain, Switzerland and Sweden) was analysed. Sorption tests were carried out both under oxic and anoxic conditions (preserved from the granite site extraction to mPIXE measurements), because retention mechanisms highly depend on RN speciation, and the same element under different oxidation states can be mobile or immobile.

Results showed that uranium retention on granite surface was heterogeneous and quantitative distribution coefficients (Ka) on selected minerals were obtained by PIXE spectra analyses. Higher sorption values were generally observed on Fe-bearing minerals, but non-zero values were measured on most of the minerals. Values measured under both redox conditions are compared.

The research leading to these results has received funding from EU Seventh Framework Programme (FP7/2007-2011) under the grant agreements № 269658 (CROCK, Crystalline Rock Retention Processes and № 2620109 (ENSAR, European Nuclear Science and Applications Research).

PC16

BEHAVIOR OF POLYACRYLAMIDE FLOCCULANTS AND ACRYLAMIDE IN MODEL CLAYS AND SOILS

Mnif I.[1], Hurel C.[1], Guezennec A.G.[2], Marmier N.[1]

[1]University of Nice Sophia Antipolis, ECOMERS, Parc Valrose, 28 avenue Valrose, 06108 Nice cedex 2, France
[2] BRGM, 3 Avenue Claude-Guillemin, BP 36009, 45060 Orléans Cedex 2, France

Ines.Mnif@unice.fr

Polyacrylamide-based-flocculants have been used in many fields for up to 50 years (agricultural, mineral processing, water purification and wastewater treatment). They are currently used in the treatment processes of industrial effluents as they facilitate suspended solids decantation. Flocculants are essentially formed by anionic polyacrylamide, an ultra-high molecular weight polymer, made through a polymerization process between acrylic acid and acrylamide. During the production of polyacrylamide, 0.025% to 0.05% of residual acrylamide is left in the polyacrylamide molecule. This monomer is known to be a human neurotoxin, an animal carcinogen and neurotoxin, and is believed to be a human carcinogen.

In France, the washing water used in Aggregates industry is recycled by flocculation / decantation in thickeners. Sludge obtained from the thickener underflow is discharged in settling lagoons. Even if clay material is used to ensure lagoons sealing, infiltration of flocculants in soils is expected. Considering the large amount of sludge generated by this industry (up to 50 tons of sludge, containing up to 100 g/t, of flocculants), interactions between flocculants and mineral and/or organic soils phases have to be studied. On the other hand, very little is known about the fate, the degradation and the transport of polyacrylamide and acrylamide in long term storage context.

The aim of this research is to examine the fate and the transport of acrylamide and anionic polyacrylamide used as flocculants in Aggregates industry. For that, a series of laboratory and numerical experiments will be conducted including: 1) batch experiments for measuring sorption levels and kinetics, for the acrylamide and polyacrylamide, on model clays and the natural solid phase from the host site; 2) numerical simulations for the transport of both acrylamide and polyacrylamide in soil.

PC17

SPECIATION OF CADMIUM USING DGT SENSORS IN QUASI-EQUILIBRIUM CONDITIONS

Mongin S.[1]*, Uribe R.[1,2], Rey-Castro C.[1], Cecília J.[2], Galceran J.[1], Puy J.[1]

[1]Departament de Química Universitat de Lleida, Rovira Roure 191, 251698, Lleida, Spain
[2]Departamento de Física, Universidad del Tolima, Ibagué, Colombia
[3]Departament de Matemàtica, Universitat de Lleida, Rovira Roure 191, 251698, Lleida, Spain

sandrine.mongin@quimica.udl.cat

DGT (Diffusive Gradients in Thin Film) is a dynamic analytical technique based on a metal binding material that disturbs the distribution of metal species in a layer adjacent to the sensor. The typical equation linking the amount of metal measured by DGT to the so-called "DGT-concentration" (related to the amount of labile species) in the medium relies on several assumptions [1]. A key one is that the surface of the resin layer acts as a perfect sink, corresponding with the concept that the binding is irreversible, almost instantaneous and the accumulated metal amount is much lower than the resin capacity. Experimental observations show that DGT does not work well at low pH [1-4], due to proton competition [5]. In these cases, the metal binding equilibrium with the Chelex resin in the DGT sensor could be approached. Accordingly, the free metal concentration at the resin-gel interface is not zero and the linearity of the accumulated mass versus time is lost. A similar situation is found in presence of ligands with an affinity for the metal similar to that of the Chelex.

The present study describes how the metal accumulation by DGT sensors is affected in presence of competitors (protons and ligands), from a combined experimental / modelling perspective. A numerical model considering that the species can penetrate into the resin layer [6] is applied to describe the accumulation of cadmium by DGT sensors and validated with a series of experiments in controlled conditions (pH, ligand concentration, temperature, etc.).

The results show that the approach to equilibrium of the metal-resin binding can exert a significant influence on the experimental metal accumulations measured by DGT, even at relatively short deployment times, depending on the conditions of the immersion solution (pH, concentration of ligand…). This influence can lead to an underestimation of the "labile" metal concentration in the system, if the resin layer was taken to act as a perfect sink. On the other hand, if the equilibrium is reached, the free metal concentration present in the solution can be determined.

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PC18

IMAGE ANALYSIS APPLIED TO LONG-TERM MONITORING OF BIOFILMS

Adouani N., Pons M.N.*, Alnnasouri M. , Pontvianne S.

Laboratoire Réactions et Génie des Procédés – CNRS, University of Lorraine, BP 20451, 54001 Nancy cedex, France

marie-noelle.pons@univ-lorraine.fr

In natural (rivers, etc) as well as in engineered systems (wastewater and water treatment) bacteria are often organized as biofilms. The life cycle of biofilms can be viewed as a sequence of periods of development and detachment, which are related to many factors such as food availability or hydrodynamical stress. The monitoring of biofilm life cycle over long periods of time with limited interference of the sensing devices is not easy. For several years now we have developed tools based on image analysis of transparent or opaque coupons which can be exposed to various aquatic environment. These coupons can be briefly removed from their environments, scanned and put back in place. The image analysis is based on distributions of image grey levels (histograms) that can be related, under certain conditions, to biofilm mass and/or thickness and texture descriptors that can be related to events or macrostructure features: detachment, auto-digestion, denitrification (bubbles). Texture descriptors are provided by algorithms such as Grey Level Runs Length (GLRL) method that provide information on pixel positions.

Among the tested applications, a two-year biodiscs lab system fed with real wastewater has been monitored. The transparent biodiscs (diameter = 10 cm, rotation speed = 5 rpm) are used as coupons. They are removed from the reactor every two days in average and scanned. The reactor liquid phase is also analysed with respect to nitrogen species (N-NH_4 and N-NO_3) and dissolved carbon. Figure 1 shows the variation of the average grey level and its standard deviation for three discs. From the information extracted from such data, the phase length and the simultaneity of detachment events can be studied.

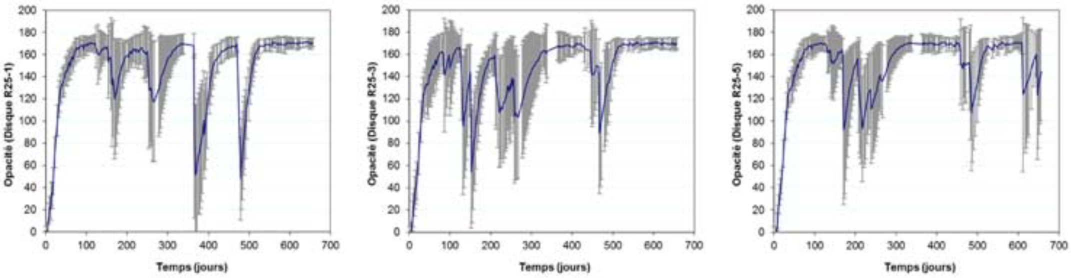

Figure 1: Evolution of biofilm in a long-term biodisc experiment.

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PC19

COMPETITIVE SORPTION INVOLVED IN WASTERWATER TREATMENT: CONTRIBUTION OF TITRATION CALORIMETRY TO THE UNDERSTANDING OF COMPETITIVE MECHANISMS

Prelot B.,* Marchandeau F., Zajac J.

Institut Charles Gerhardt de Montpellier, CNRS UMR 5253, Université Montpellier 2
Equipe Agrégats, Interfaces et Matériaux pour l'Energie, C. C. 1502,
Place Eugène Bataillon, 34095 Montpellier cedex 5, France.

prelot@um2.fr

Solid-liquid interfacial phenomena, involved in the industrial implementation of any separation or environmental technology, always occur under conditions of competition among the variety of ionic or molecular species present in the system. From a fundamental viewpoint, it is highly inappropriate to study the interfacial mechanisms only in the presence of a single solute in solution since the competitive phenomena do not necessarily follow the same reaction patterns. Concerning the solid sorbents available from commercial sources or produced in laboratories, their properties inferred from tests carried out under ideal conditions rarely reflect their behaviour in real multi-component systems. One of the interesting research possibilities is to study the competitive interactions of various solutes either between themselves in bulk solutions or with the solid surface. Direct measurements of the thermal effects in such systems by calorimetry can provide important indications of the mechanisms involved. Of course, calorimetry alone is not capable of solving satisfactorily many detailed problems concerning the resulting phenomena and, therefore, calorimetric measurements have to be supplemented by other experimental studies reported on the system so as to obtain a more complete description.

Some examples of the use of titration calorimetry to study the competitive interactions between different heavy metal cations or between a heavy metal cation and an organic solute in aqueous solution and at the solid-water interface will be presented. The plots of the enthalpy of displacement vs. amount adsorbed, or those of the enthalpy of dilution vs. solution composition, will be compared between single-solute and multi-component systems. The comparative adsorption studies will be also illustrated by taking into account the individual and composite sorption isotherms of the solutes analysed here. All these results will be discussed to emphasize the advantages of the calorimetric approach in studies of the competitive interfacial mechanisms.

PC20

CORRELATION BETWEEN SURFACE ENERGY AND HYDRATION PROPERTIES OF MONTMORILLONITE SATURATED WITH HEAVY METALS

Salles F.[1]*, Douillard J.M.[1], Bildstein O.[2], Prelot B.[1] Van Damme H.[3]

[1]Institut Charles Gerhardt Montpellier, UMR CNRS 5253, UM2, ENSCM, Place E. Bataillon, 34095 Montpellier Cedex 05 France
[2] DEN/DTN/SMTM/LMTE, CEA Cadarache, 13108 Saint Paul Les Durance, France
[3] PPMD / ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 5, France

fabrice.salles@univ-montp2.fr

Heavy metals contamination of water resources and soils is of great concern as it poses not only severe risks to humans, but also potentially unacceptable ecological risks to plants, animals and microorganisms. Swelling clays are considered to bring valuable issues for pollutants removal [1]. The knowledge of their surface energy is found to give crucial information to understand and predict the hydration properties and retention or transport mechanisms. In our study, the structure of montmorillonites saturated with heavy metals is determined using molecular simulation. The surface energy is then estimated using electrostatic calculations as already applied for homoionic montmorillonites substituted with alkaline cations [2]. Finally, we compare the behaviour of montmorillonites saturated by either heavy metals or alkaline cations [3] and try to predict the hydration properties [4].

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PC21

INCREASED SORPTION OF TWO PESTICIDES ON A SOIL FROM A MINING AREA ADDED WITH SEWAGE SLUDGE

Rodríguez-Liébana J.A.[1]*, Peña A.[1], Mingorance M.D.[1], Leidi E.O.[2], Rossini Oliva S.[3], Valdés Castrillón B.[3], Pina Gata F.J.[3], Fernández Espinosa A.J.[4]

[1]Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), 18100-Armilla, Granada (Spain).
[2]Instituto de Recursos Naturales y Agrobiología (CSIC), 41012 Sevilla (Spain)
[3]Departamento de Biología Vegetal y Ecología, Universidad de Sevilla, 41080 Sevilla (Spain)
[4]Departamento de Química Analítica, Universidad de Sevilla, 41012 Sevilla (Spain)

joseantonio.rodriguez@iact.ugr-csic.es

Conservation and reclamation efforts to ensure beneficial use of mining areas are a social and environmental necessity. Remediation strategies must establish soil productivity as a self-sustaining ecosystem, but also the capability of remediated soil to cope with organic pollutants. Addition of amendments is considered an appropriate strategy to enhance the retention of organic pollutants, such as pesticides, reducing their transport by leaching or runoff processes.

Soil from Riotinto mining area (SW Spain), with pH 2.4 and 1.4% of organic carbon (OC), was limed to rise soil pH to physiological values, and added with sewage sludge (2, 5 and 10% w:w) from three different treatments: air-dried stabilized (SSL), composted (CSL) and composted with prune wastes (CLV). The soil was incubated at 40% field capacity for 2 months. The incubated amended soil was used to evaluate pesticide sorption with the batch technique by using mixtures of thiacloprid (THC) (insecticide, log K_{ow} 1.26) and fenarimol (FEN) (fungicide, log K_{ow} 3.69) at a single concentration (5 mg/L). Sorption distribution coefficients representing pesticide distribution between soil and liquid phases (K_d, mL/g), soil solution properties (pH, electrical conductivity, Abs, HIX) and selected soil properties were determined to help in data interpretation.

THC sorption (K_d) ranged between 1.2 and 3.9 mL/g, while that of FEN oscillated between 6.0 and 35.1 mL/g, in accordance with their physicochemical properties. Addition of a liming agent induced for both compounds a decrease in their sorption, likely due to a change in the charge characteristics of soil OC with increasing pH [1], as confirmed by the HIX values. The adsorption increased with amendment dose and with the nature of the amendment, ranged as SSL > CLV > CSL.

Pesticide sorption was significantly correlated with soil OC (rFEN = 0.857, rTHC = 0.746). The evaluation of soil solution properties indicated that absorbance at different wavelengths was higher for SSL than for the other two composted amendments, while HIX values were the lowest, confirming that SSL was the less humified sludge.

Thus the addition of organic amendments to degraded soils, such as those from mining areas, should be selected taking into consideration not only soil fertility, but also soil ability to protect the underlying saturated zone from organic pollution. Addition of SSL from urban treatment plants resulted in enhanced pesticide retention, in comparison with both composted sludges.

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PC22

SYNTHESIS OF HIGH-STRENGTH ZEOLITE MONOLITH BY STEAM-ASSISTED CRYSTALLIZATION

Tamon H.*, Aotani K., Mori H., Sano N.

Department of Chemical Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

tamon@cheme.kyoto-u.ac.jp

Zeolite is known as a catalyst or an adsorbent, and has been used in various applications. The fabrication of zeolite is extremely important for its applications. Especially, honeycomb morphology has recently attracted great attention from its low pressure drop and short diffusion length. However, it is extremely difficult to fabricate zeolite in honeycomb morphology. The authors have applied ice-templating, which consists of so-gel polycondensation, unidirectional freezing of hydrogels and freeze drying, to the synthesis of silicalite monolith [1]. In this work, the high-strength zeolite monolith is synthesized by ice-templating and steam-assisted crystallization (SAC) by using a structure-directing agent (SDA).

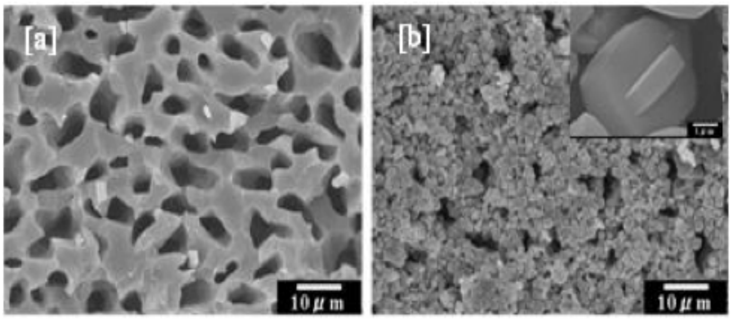

Fig. 1 SEM images of precursor silica gel [a] and sample after crystallization [b]. Inset image in [b] is magnified view of synthesized particulate crystal.

The precusor silica gel was prepared by applying the ice-templating to the hydrogels synthesized from colloidal silica. The zeolite monolith with three-dimensionally interconnected macropores was synthesized by SAC of the precursor silica gel by using tetrapropylammonium hydroxide as SDA.
The zeolite monolith has the continuous macropores, and the surface of these macropores is densely covered with silicalite-1 crystals as shown in Fig. 1. Silicalite-1 crystals have a well ordered microporous structure. Since the macropores, which were formed by ice-templaing, are directly connected to the micropores of the synthesized silicalite-1 crystals, the synthesized zeolite monolith have the hierarchical structure of macropores and micropores. The BET surface area of zeolite monolith increases up to 355 m^2/g by the steam-assisted crystallization, and the samples with crystallinity beyond 90 % has high compressive strength of 5-12 MPa. The zeolite monolith shows low pressure drop, and the pressure drop of the sample is one-twentieth of that of the packed-bed of particles.

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PC23

THE MODIFICATION EFFECTS ON THE PORE STRUCTURE PROPERTIES OF ACTIVATED CARBON FOR THE ADSORPTION OF PHENOL.

Temdrara L.[1,2]*, Khelifi A.[2], Addoun A.[2]

[1]Faculté des Sciences, Université Hassiba Benbouali, BP.151, Chlef 02000, Algérie.
[2]Laboratoire d'Etude Physicochimique des Matériaux et Application l'Environnement, Faculté de Chimie, U.S.T.H.B., BP.32, El-Allia, 16111 Bab-Ezzouar, Alger, Algérie.

temlarbi@yahoo.fr

In this work, several activated carbons were prepared by the activation of the olive stones by various rates of $ZnCl_2$ [1]. The activated carbon CA3 is treated by nitric acid solution with differents concentration [2]. The results obtained show that the porous texture of the activated carbon is all the more developed that the rate of the activating agent ($ZnCl_2$) is higher; as example, the specific surface, determined by method B.E.T., of the CA3 reaches the value of 1860 m^2/g. For oxidized carbons, the surface area and the enthalpy of immersion are decrease when the concentration of HNO_3 increases. The adsorption of phenol on various coals showed us that the phenol adsorption capacity is faster in the following order: CA3 > COx1> COx2. The fixing of the functions of surface obstructs the diffusion of the molecules of phenol with in internal porosity. This diffusion is all the more important as the number of these functions increases (case of COx2).

Key words: enthalpy of immersion, activated carbon, adsorption, phenol.

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MODIFICATION OF THE GENERIC NICA-DONNAN MODEL PARAMETER FOR THE MODELING OF EU BINDINGS BY DEEP GROUNDWATER HUMIC SUBSTANCES

Terashima M.[1]* , Saito T.[2], Iijima K.[1], Yui M.[1]

[1] Geological Isolation Research and Development Directorate, Japan Atomic Energy Agency (JAEA), 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki, 319 – 1194, Japan.
[2] Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113 – 8656, Japan.

terashima.motoki@jaea.go.jp

Modeling of radionuclide bindings by deep groundwater humic substances (HSs) is essential for assessing effects of HSs on migration of radionuclides in geological disposal system of high level radioactive waste. The Non-Ideal Competitive Adsorption (NICA)-Donnan model of which generic parameters have been prepared [1, 2] is one of the most useful models for the modeling of metal-ion bindings by HSs in a variety of solution conditions. However, its application can be limited depending on the origins of HSs used for the generic parameters. In previous study, we have shown that the NICA-Donnan model can successfully simulate the Eu solubility in the presence of Aldrich humic acid (HA), but not in the presence of the deep groundwater HSs in Horonobe area, Hokkaido, Japan [3]. This disagreement between the experiments and the simulations could be due to the difference between generic and specific parameters, because the model parameters can depend on the structural characteristics of HSs. Thus, the generic parameter needs to be modified for better modeling of metal-ion bindings by HSs in a given environment. In this study, to modify the generic parameters, specific proton binding parameters of the deep groundwater HSs in Horonobe area were used instead of the generic proton binding parameters, and its effectiveness was investigated on the basis of comparison between experimentally obtained Eu^{3+} binding data and simulations using the new parameters.

Based on the comparison between experiments and simulations, it was found that the application of the specific proton binding parameters improved the applicability of the NICA-Donnan model for the modeling of Eu^{3+} bindings by the deep groundwater HSs. In particular, Eu^{3+} bindings by deep groundwater fulvic acid (FA) as a function of pH at different ionic strengths were successfully simulated by the NICA-Donnan model using the specific proton binding parameters. This indicates that the application of specific proton binding parameters can successfully improve the description of the competitive reaction with proton and electrostatic interaction in the Eu^{3+} binding by the deep groundwater FA. On the other hand, for the deep groundwater HA the application of specific proton binding parameters had limited effectiveness against the optimization. This indicates that characteristics of binding sites for deep groundwater HA may be different from those of general HA that is described by the generic parameters. Therefore, specific metal-ion binding parameters should be used for the modeling of radionuclide bindings by the deep groundwater HA.

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ELECTROCHEMICAL REDUCTION OF CO_2 TO ORGANIC ACID BYA PD/MWNTS GAS-DIFFUSION ELECTRODE IN AQUEOUS MEDIUM

Wang H.[1]*, Lu G.[1], Bian Z. Y.[2], Wang H. J.[1]

[1] College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, PR China
[2] College of Water Sciences, Beijing Normal University, Beijing 100875, PR China

wanghui@bjfu.edu.cn

Climate change and energy shortage have drawn much more attentions. Carbon dioxide is believed to be the largest contributor to greenhouse efforts [1]. So the work on the viable usage of carbon dioxide as carbon source for useful fuels in the framework of attempts to lessen emissions of carbon dioxide into atmosphere is urgent. Much research has been made on the electrochemical reduction of carbon dioxide, because it not only decreases the amount of carbon dioxide, but also produces a variety of useful organic compounds [2]. Pd/multi-walled carbon nanotubes (MWNTs) catalysts for conversion of CO_2 to organic acids were prepared by glycol reduction, and characterized by fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and cyclic voltammetry (CV) technology. The amorphous structure Pd particles with an average size of 9.17 nm were highly dispersed on the surface of carbon nanotubes. The electrochemical reduction of CO_2 was investigated in a diaphragm electrolysis device, using Pd/MWNTs gas-diffusion electrode as a cathode and a $Ti/IrO_2/RuO_2$ net anode. The main products in present system were formic acid and acetic acid identified by ion chromatograph. High electrocatalytic activity of Pd/MWNTs for the CO_2 conversion appeared. The maxium faradaic efficiencies of fomic and acetic acid formed on the Pd/MWNTs gas-diffusion electrode at 4 V under CO_2 1 atm were 21.6 and 42.3%, respectively, in 0.5 and 0.8 mol L^{-1} $KHCO_3$.

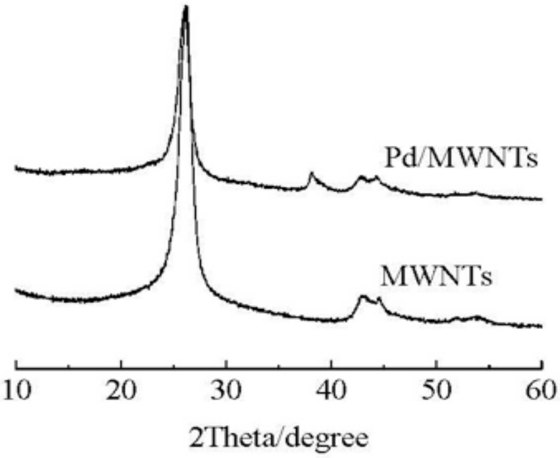

Fig. 1. XRD pattern of MWNTs and Pd/MWNTs catalysts.

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PC26

TYLOSIN SORPTION AND THERMODYNAMICS ON MINERALS

Zhang Q.[1], Guo X.T.[1], Yang C.[1]*

[1]College of Environmental Science and Engineering, South China University of Technology, Guangzhou, China
510006

cyanggz@scut.edu.cn

Tylosin (TYL), as an organic base with pK_b value of 7.1, is positively charged in acidic solution and neutral under alkaline conditions. Hence, mineral is considered to affect its environmental behavior. Previous study about tylosin sorption on soil, shown that tylosin sorption was positive relation with the clay content of soils. Therefore, the purpose of this study was to primarily investigate the sorption characters on minerals at different temperatures. In this study, montmorillonite, kaolinite, and goethite were chose as the sorbents on base of the mineral composition of the study soils. The completely mixed batch reactor (CMBR) systems were used in the experiment. Sorption isotherms at different temperature were measured under a range of solution condition. Freundlich isotherm model was used to fit the sorption data. The result showed that all of the sorption isotherms were nonlinear. The sorption capacity followed the order of montmorillonite > Goethite > kaolinite. The surface charge, surface area and activity of hydroxyl could explain the distinction among the three minerals. Thermodynamics of sorption can be concentration-dependent. However, the current approach obtains thermodynamic information by conducting sorption experiment only at a single concentration point, which may be of limited used. As a result, thermodynamic parameters at different concentration were discussed in this study. Analysis of the thermodynamic parameters showed that tylosin sorption on three minerals was spontaneous, thermodynamically favorable, and exothermic. The site energy distribution indicated that the sorption sites with lower site energies were more heterogeneous. Temperature may affect the sorption site heterogeneity because of the different structure of minerals.

SESSION D:

ENVIRONMENTAL COLLOIDS AND INTERFACES: PROPERTIES, STRUCTURE, REACTIVITY

ID1

Session D: Environmental colloids and interfaces : properties, structure, reactivity

PHYSICOCHEMICAL DYNAMICS OF AQUATIC NANOPARTICULATE METAL COMPLEXES

Van Leeuwen Herman P.

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen,
The Netherlands

herman.vanleeuwen@wur.nl

Recent progress in our understanding of the chemodynamics of aquatic metal complexes with nanoparticulate and colloidal complexants is evaluated and put in perspective.

The basic steps in the complex formation process, i.e. diffusion of the reactants to form ion pairs and the eventual inner-sphere complex formation, are revisited and further developed for particles with or without electric charge. In the nanoparticulate size range, we pay special attention to the case of environmental fulvics for which the electrostatic and electrodynamic effects are generally large. Complexation of metal ions with the larger soft and/or hard colloidal ligands is characterized by low rates of diffusive reactant metal ion transport. The complex formation/dissociation rate constants can be shown to decrease with increasing particle radius, thus giving rise to longer equilibration times and lower labilities.

A peculiar feature of negatively charged nanoparticulate ligands is that complexing metal ions not only react with binding sites but also accumulate at the particle surface (hard case) or inside its body (soft case). For ionic strengths where the Debye length is similar to the particle radius, the extraparticulate part of the electric particle/medium double layer hosts a significant part of the particle-associated metal ions. This has consequences for the magnitude of the rate of inner-sphere complex formation with sites inside the particle body.

Another feature of charged nanoparticulate ligands is that they significantly modify the rate of diffusion of ions to/from the particle body. For negative charges, the diffusion of positive metal ions towards the particle is enhanced by a conductive acceleration, the extent of which depends on the magnitude and extension of the electric field generated at the particle/medium interface. By elaborating on a classic approach of rates of ionic reactions by Debye, a quantitative theoretical analysis for this acceleration by dispersed particles has recently been proposed. Implementation of the various ideas in the interpretation of experimental complexation data for colloidal and nanoparticulate complexes is still in its childhood.

KD1

SIZE AND ELEMENTAL ANALYSES OF NANO-COLLOIDS IN DEEP GRANITIC GROUNDWATER: IMPLICATIONS FOR TRANSPORT OF TRACE ELEMENTS

Saito T.[1*], Mizuno T.[2]

[1] Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo
[2] Horonobe Underground Research Center, Japan Atomic Energy Agency

takumi@flanker.n.t.u-tokyo.ac.jp

Natural colloids in subsurface environments can mediate the migration of contaminants as carriers [1, 2]. Our understanding on such colloid-mediated transport of contaminants is, however, limited to shallow underground environments. Deep underground, which is suitable for geological disposal of nuclear wastes, possesses rather different chemical and biological environments from those of earth's surfaces or shallow undergrounds. Thus, colloids in deep groundwater are likely to be different as well, although our knowledge on which components of given groundwater mediate the migration of contaminants and how they do it is still premature, largely because of limited availability of deep groundwater samples.

In this study, groundwater samples collected at -300 m below ground level were analyzed with respect to the size distributions of colloids and their elemental compositions by field-flow fractionation (FFF) and inductively coupled plasma mass spectroscopy (ICP-MS). The sampling site was the Mizunami underground research laboratory operated by the Japan Atomic Energy Agency [3]. The basic geology around the sampling location was fractured granite rocks and the groundwater was Na-(Ca)-Cl type having pH around 9. The size distributions of organic colloids after FFF fractionation were measured by online UV/Vis and fluorescence detectors and those of inorganic elements by ICP-MS connected to the outlet of the fluorescence detector. Major elements such as Al and Fe together with organic colloids were considered as host colloidal phases. Meanwhile, trace elements such as heavy metals, lanthanides and actinides were considered as guest constituents of the colloids. The correlation of the size distributions between the major and trace components was used to elucidate the roles of deep groundwater colloids as carriers of trace elements.

Organic colloids detected in a groundwater sample exhibited a narrow size distribution around 2 nm. Various inorganic elements were detected below 40 nm, a part of which had similar size distributions as those of the organic colloids (Zn^{2+} and Cu^{2+}). Based on the correlation between the size distributions, Sr^{2+} was found to be associated with Ca^{2+}, probably forming solid solution in $CaCO_3$. It was also shown that the size distributions of lanthanide elements correlated with that of Al^{3+} and that uranium (either as UO_2^{2+} or U^{4+}) and Th^{4+} existed in the same size ranges as either organic colloids or Al^{3+}. Similar results were obtained for the other groundwater samples collected nearby, suggesting that certain colloids such as organic colloids, calcite and colloids containing Al^{3+} served as carriers of the trace elements in the investigated groundwater samples.

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Session D: Environmental colloids and interfaces: properties, structure, reactivity

RD1

OCCURENCE OF NANO-SIZED, DISPERSED FERRIHYDRITE AGGREGATES IN SOIL EFFLUENTS

Fritzsche A.[1*], SchröderC.[2] , Rennert T.[3], Wieczorek A.K.[1], Händel M.[1], Totsche K.U.[1]

[1]Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, D-07749 Jena, Germany
[2]Universität Bayreuth, Eberhard-Karls-Universität Tübingen, D-72074 Tübingen, Germany
[3]Lehrstuhl für Bodenkunde, Technische Universität München, D-85350 Freising, Germany

a.fritzsche@uni-jena.de

When Fe^{2+} is oxidized in nature at neutral pH, ferrihydrite precipitates and generally forms micron-sized aggregates. Such coarse particles settle down in aqueous phase and reduce the mobility of Fe and that of associated species, e.g. nutrients like P and contaminants like As. However, a proceeding ferrihydrite aggregation was interrupted under conditions that can be expected at anoxic-oxic interfaces in soils, which resulted in the formation of nano-sized, dispersed ferrihydrite aggregates. These ferrihydrite colloids from soil-derived solutions effectively bind As [1] and are readily dissolved by microbial Fe(III)-reduction [2]. Consequently, the occurrence of ferrihydrite colloids affects the activity and reactivity of soils and the elemental cycling within soils. The present study focuses on size, composition, structure and surface properties of the ferrihydrite colloids and the relation between those properties and the composition of the soil-derived solution from which the colloids had precipitated.

Soil columns were filled with material from the topsoil horizons (Ah, Ap) of a gleyic Fluvisol and stagnic Luvisol, respectively, and operated under water-saturated conditions. The respiration of soil microorganisms induced anoxic conditions within the soil columns and consequently the accumulation of Fe(II) in the soil solution owing to the reductive dissolution of pedogenic Fe oxides. The column effluent was re-aerated after its discharge resulting in the oxidation of Fe(II) and the precipitation of Fe oxides. With the exception of a low ionic influent (10^{-3} M NaCl), nothing further was introduced into the soil columns. Thus, the observed processes in the soil effluent can be expected to occur at anoxic-oxic interfaces in the (soil) environment. Mössbauer spectroscopy and XRD revealed the formation of poorly ordered ferrihydrite. Its crystallization was disturbed by (in)organic species that have associated with ferrihydrite. FTIR spectroscopy pointed to mainly polysaccharides, carboxyls, proteins and aromatics as available organic compounds. The aggregation decreased with decreasing effluent ionic strengths and higher organic carbon/Fe ratios. Dynamic light scattering revealed aggregate sizes as low as 50 nm, which was confirmed by AFM and SEM. The size of these ferrihydrite nanoaggregates remained constant for at least several weeks. Independent of actual dimensions, similar physical properties of the aggregate surfaces were detected.

This study demonstrated the reproducible, long-term stabilization of ferrihydrite colloids in complex solutions derived from various topsoil horizons. The soil cation exchange capacity and the amount of water-soluble organic matter in relation to the amount of microbially available pedogenic Fe oxides determine the intensity of ferrihydrite aggregation and therefore the size of its aggregates.

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RD2

DETERMINATION OF SURFACE PROPERTIES OF VIRAL PARTICLES: A CHALLENGE TO EXPLAIN THEIR FATE IN AQUATIC MEDIA

Gantzer C.*, Dika C. and Duval J. F. L.*

* C. Gantzer: Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), Université de Lorraine, CNRS, 5 Rue Albert Lebrun, F-54250 Nancy, France. E mail: Christophe.Gantzer@pharma.uhp-nancy.fr.
* J. F. L. Duval: Laboratoire Environnement et Minéralurgie (LEM), Université de Lorraine, CNRS,
15 Avenue du Charmois, 54501 Vandoeuvre-Les-Nancy, France.

Christophe.Gantzer@pharma.uhp-nancy.fr - Jerome.Duval@ensg.inpl nancy.fr.

MS2, Qb and GA phages of diameter 20-30 nm belong to the *Leviviridae* family) and are classically used as model systems to describe the fate of pathogenic enteric viruses in the environment. These particles are paradigms of soft bioparticles because their structure consists of three permeable concentric and charged layers that differ in composition: a bulk RNA region, an RNA protein-bound layer, and a proteic capsid that forms the outer shell of the virus. The determination of the commonly named 'surface properties' of viruses is crucial for understanding their adhesion onto biotic or abiotic substrates or their stability with regard to aggregation processes. Such analysis should at least allow the estimation of the charge carried by the viruses as well as their hydrophilic/hydrophobic balance. In this context, the sole consideration of isoelectric point of viruses and the use of standard DLVO model were shown to be of limited applicability for e.g. explaining the adhesion/aggregation properties of viral particles. In particular it was evidenced that internal RNA has a significant impact on the electrokinetic properties and on the aggregation of the phages (Dika *et al.* 2011). The permeability of phages to external flow should be taken into account to quantitatively estimate the level of global charge carried by the virus from electrophoretic mobility measurements. Soft particles concept was therefore applied to define the electrokinetic properties of different bacteriophages (Langlet *et al.* 2008a) and no significant difference was found for estimated charge and permeability of the three kinds of bacteriophages of concern. Different approaches for evaluating the hydrophobicity of particles evidenced the following hydrophobicity sequence, MS2<Qb<GA phages (Langlet *et al.* 2008b) where '<' means 'less hydrophobic than' Differences in the hydrophilic/hydrophobic balance between the phages highly impacted their behavior during a water treatment by coagulation-flocculation and ultrafiltration (Boudaud *et al.* 2012) and was further found to govern their adhesion onto different surfaces defined by various roughness and hydrophobicity degrees.

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RD3

CHEMODYNAMICS OF METAL COMPLEXATION BY NATURAL HETEROGENEOUS SOFT COLLOIDS

Town R. M.[1]*

[1] Institute for Physics, Chemistry, and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense, Denmark

rmt@ifk.sdu.dk

Humic substances (HS) are natural heterogeneous complexants that are ubiquitous in soils and natural waters. They range in size from oligoions (fulvic acid) with radius of order 1 nm, to small permeable nanoparticles (humic acid), with radius of a few nm. HS carry a significant negative charge at ambient pH and they are important complexants of metal ions in the environment. A characteristic feature of HS is their heterogeneity which gives rise to distributed thermodynamic and kinetic properties. For predictions of the dissociation rate of metal complexes with HS (and ensuing lability at a given timescale), the usual approach is to assume that the rate of association is invariant and limited by the rate of metal dehydration. However, this assumption yields dissociation rate constants that are significantly greater than those determined experimentally.

New insights into the chemodynamics of metal ion complexation by HS are obtained by application of recently developed theory for permeable charged nanoparticles [1-3]. Two opposing electric effects are operational with respect to the overall rate of association, namely (i) the accelerating effect of the negative electrostatic field of the humic particle on the diffusive transport of metal ions towards it, and (ii) the extent to which metal ions accumulate in the negatively charged particle body as determined by the ionic Boltzmann equilibration with the medium. To identify the rate-limiting step in the metal-humic complex formation process, theoretical values of the rates of outer-sphere and inner-sphere complexation are compared with those derived from measurements of the thermodynamic stability constant (K) and the dissociation rate constant (k_d). For the case of rapidly dehydrating metal ions, e.g. Cu(II), the experimentally derived association rate is in good agreement with the theoretical rate of outer-sphere association, in contrast with the general assumption that inner-sphere dehydration is the rate-limiting step in metal-humic complexation. Furthermore, the association rate is found to be practically independent of the degree of metal ion complexation, which confirms previous assumptions that the distribution in K is reflected in that of k_d. The results are highly significant for interpretation of chemodynamics of metal complexation by HS.

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RD4

MECHANISMS OF FORMATION AND REACTIVITY OF IMOGOLITE TYPES MATERIAL

Rose J.[1,2]*; Levard C.[1,2]; Thill A[2,3]; Masion A.[1,2], Chaurand P.[1,2]; Doelsch E.[4], Basile-Doelsch I.[1], Bottero J-Y.[1,2]
[1] CEREGE, CNRS-UPCAM UMR6635 13545 Aix en Pce Cedex 04-France,
[2] International Consortium for the Environmental Implications of Nanotechnology, iCEINT,France.
[3]CEA, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanometrique et Supramoleculaire,
91191 Gif-sur-Yvette, France.
[4]CIRAD, UR Recyclage et Risque, Saint-Denis Messagerie Cedex 9, La Réunion, F-97408 France.

rose@cerege.fr

Reactivity of nanoparticles represents a central issue for many laboratories around the world. Among many supported efforts the control of the morphology of nanoparticles is motivated by the fact that morphology strongly influence the properties of the final products. Among the vast family of available nanoparticles, imogolite is a clay nanotube for which perfect control of the diameter is possible. Imogolites were first observed in volcanic soils[1]. They are natural aluminosilicate nanotubes having the general formula (OH)3Al2O3SiOH with a 2 nm external diameter and up to micrometers in length. The impressive monodispersity in imogolite nanotube diameter has motivated research on their formation mechanism. Synthesis protocols to produce imogolite were quickly developed. Farmer et al. were the first to obtain synthetic imogolite using low concentrations of $AlCl_3$ and SiO_2 monomers as starting materials (millimolar concentrations of the reagents) [2]. However, the production of large amount of imogolite or imogolite type materials remained challenging for long time. We will present our most recent results concerning the possibility to produce imogolite type materials from highly concentrated stock solutions. We will also detail the possibility to form double wall Al-Ge nanotubes and the different stages of their formation [3-7]. We will then detail the surface reactivity of these nanotubes toward metals at he lab scale as well as in natural soil.

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RD5

SOFT BIOLOGICAL INTERFACES: PHYSICO-CHEMICAL PROPERTIES INVESTIGATED BY ATOMIC FORCE SPECTROSCOPY

Francius Grégory[1], Polyakov Pavel[1,2], Abe Yumiko[1], Krapf Marie-Eve[2], Skali-Lami Salah[3], Block Jean-Claude[1], Lartiges Bruno[2,4], Ghigo Jean-Marc[5], Beloin Christophe[5] and Duval Jérôme F.L.[2]

[1]LCPME, Université de Lorraine, CNRS UMR 7563, 405 rue de Vandoeuvre 54600 Villers-lès-Nancy, France.
[2]LEM, Université de Lorraine, CNRS UMR 7569, B.P. 40, F 54501 Vandoeuvre-lès-Nancy, France.
[3]LEMTA Université de Lorraine, CNRS UMR 7563, 2 avenue de la Forêt de Haye B.P. 160, F-54504 Vandoeuvre-lès-Nancy, France.
[4]GET, Université Paul Sabatier, CNRS UMR 5563, 14 avenue Edouard Belin, F-31400 Toulouse, France.
[5]Institut Pasteur de Paris, Groupe de Génétique des Biofilms, CNRS URA 2172, 25-28 rue du Docteur Roux, F-75015 Paris, France.

gregory.francius@lcpme.cnrs-nancy.fr

Adhesion of bacteria plays an important role in the biocolonization of biotic and abiotic surfaces. The resulting formed biofilms represent important financial losses e.g. in water treatment industry, and further potentially constitute a major risk to public health. Several studies have evidenced that the propensity of bacteria to deposit onto surfaces and form biofilm is intimately connected to their nanoscale surface properties (surface structure, electrohydrodynamics, hydrophobic/hydrophilic balance, etc). These properties are also known to impact interfacial processes where bioparticles are involved, e.g. polymer-mediated bioflocculation in waster water sludge treatment , response to osmotic stresses or resistance to antibacterial molecules. In this context, atomic force microscopy (AFM) has become a powerful tool for investigating at the nanoscale, surface forces, mechanical properties of deformable particles like bacteria, biomolecular interactions, kinetics and dynamics of complex biointerfacial processes. In this presentation, we exposed the potentialities of this technique for analyzing the physico-chemical properties of bacterial surfaces and biofilms via the explcit discussion of three case studies. (i) We evidenced the formation of a conditioning layer with an increase of hydrophobic forces during drinking water biofilm formation [1] and the latter is mainly composed of layered bacterial aggregates. The elastic modulus of such biomaterials we estimated to 200-5000 kPa and the mechanical detachment occurred generally for shear stress of about 100 kPa for agregates volume greater than 200 μm^3[2]. (ii) We investigated the impact of polyethyleneimine on *Shewanella oneidensis* MR-1 lacking or not the lipopoly-saccharide (LPS) O-antigen surface structure during flocculation tests [3]. (iii) We studied the influence of external bacterial cell wall structures (short and rigid Ag43 adhesins, longer and more flexible type 1 *fimbriae* and *F pilus*) on the physicochemical properties when *Escherischia coli* cells were subjected to an osmotic and ionic stress [4-5].

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RD6

COLLOID GENERATION FROM FERRIHYDRITE MACROAGGREGATES BY ORGANIC COMPOUNDS ENHANCES MICROBIAL REDUCTION RATES

Braunschweig Juliane[1]*, Bosch Julian[1], Fritzsche Andreas[2], Totsche Kai U.[2],

[1] Helmholtz Zentrum München, Institut für Grundwasserökologie, Ingolstädter Landstr. 1, D-85764 Neuherberg
[2] Friedrich-Schiller-Universität Jena, Institut für Geowissenschaften, Wöllnitzer Str. 7, D-07749 Jena

juliane.braunschweig@helmholtz-muenchen.de

Microbial iron reduction is a major process in groundwater ecosystems and often associated with the degradation of organic contaminants. Yet the high crystallinity and low solubility of iron oxides leads to slow reduction kinetics. In contrast, natural iron oxide colloids are highly reactive due to the large specific surface area and their association with natural organic matter (NOM). Occurrence of organic ligands (e.g. citrate) in soils, excreted by plant roots under iron deficiency, leads to iron oxide dissolution and therefore to a higher bioavailability of iron.

The objective of this work was to compare the reactivity of natural ferrihydrite colloids with synthetic ferrihydrite colloids and macroaggregates. In abiotic experiments the dissolution processes of synthetic ferrihydrite by dissolved Na3-citrate were investigated. Anaerobic reduction experiments with *G. sulfurreducens* and synthetic ferrihydrite were performed to asses the impact of dissolved Na3-citrate on microbial iron oxide reduction.

The rate of microbial reduction of natural colloids (50.9 µM h^{-1}) was two orders of magnitude higher than compared to pure synthetic ferrihydrite colloids (0.8 µM h^{-1}). When synthetic colloids were coprecipitated with citrate, iron reduction was accelerated to rates in the range of natural colloids (12.1 µM h^{-1}). Low reduction rates of pure ferrihydrite colloids were attributed to the fast aggregation and loss of colloidal properties. Abiotic incubation with ferrihydrite macroaggregates and Na_3-citrate at pH 6.5 proved the partial disintegration of ferrihydrite due to chelation of ferric iron. The production of colloids with hydrodynamic diameters between 610 (±147) nm and 105 (±6) nm from the macroaggregates was confirmed. This led to a 7-fold increase of microbial reduction rates.

We conclude that steric stabilization of colloidal ferrihydrite by organic acids, a possible colloid production from corresponding macroaggregates, and chelation of iron strongly enhances microbial iron oxide reduction.

Session D: Environmental colloids and interfaces: properties, structure, reactivity KD2

NEUTRON DIFFRACTION IN EARTH AND ENVIRONMENTAL SCIENCES

Cuello Gabriel

Institut Laue Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France

cuello@ill.eu

The increasing world population density, together with global urbanisation and industrialisation are putting a real strain on the planet and the environment. To keep on growing and prospering, or simply maintain a liveable standard of living, countries need to minimise this strain and protect their environment. Neutrons, thanks to their multiple applications and the tremendous capabilities for analysis that they offer, can contribute to the development of clean technologies and processes. They can also provide much needed insight into Earth processes and the properties of rocks and minerals.

Neutrons can be applied to several fields of Earth sciences. They provide a unique tool for the understanding of both surface and deep Earth processes. In the former case, which is dominated by the effects of water, the sensitivity of neutrons to hydrogen allows precise measurements to be made of the structure, synthesis and dynamics of hydrous mineral phases. In the latter case, which utilises the penetrating power of neutrons to study large volume samples coupled with the sensitivity of neutrons to light atoms, the field can be subdivided into either petro-physics, the understanding of the properties of rocks at high temperatures and pressures, or mineral physics, the detailed study of the individual constituent mineral phases. In space, neutrons can help detect water on planets and also make possible the study of comet cores via earth hydrates and the study of meteorites via earth ice.

Neutron diffraction can also contribute to atmospheric science and the study of ice crystals in clouds, and give valuable insight into the role of clouds in global warming. Neutrons have their role to play in the battle to minimise carbon emissions. One area in particular is in the manufacture of cement, which contributes 5-7% of man-made (and 4% of total global) CO_2 emissions. Neutron scattering techniques can help understand the process of cement aging – and thereby help to extend the lifetime of cement. This will in turn reduce overall cement production requirements and the carbon emissions it engenders. Small angle neutron scattering can also be used to analyse materials for carbon capture and storage, another way to reduce CO_2 emissions into the atmosphere. Research into alternative energy sources can also benefit from neutron scattering techniques: hydrogen storage, solar cells are only a few of the technologies that neutrons are contributing to develop.

Neutrons scattering is helping scientists to fight pollution and develop environmentally friendly processes that generate and release fewer contaminants into the environment. Neutron activation analysis and prompt gamma activation analysis can provide information about rare elements and serve as a way to detect contaminants. Neutron reflectometry and neutron diffraction can help define the intrinsic nature of pollutants and its relationship with the substance they are polluting. Neutrons are able reveal the short-range order of ions sequestered in minerals like clays. In particular, when the clays are in contact with water neutrons can determine the hydration of these ions, a key element to determine whether the ions could be released in nature or not. This is true for any pollutant, but it is particularly pertinent for actinides in nuclear repositories.

In this talk we will present several examples of the use of neutrons in environmental sciences in general, but we will mainly focus in the neutron diffraction with isotopic substitution technique, extremely useful to determine the short-range order of aquaions in confined systems. The pair distribution analysis will be also introduced and discussed.

RD7

COLLOIDAL COPPER MOBILISATION FROM VINEYARD SOILS BY FIELD-FLOW FRACTIONATION

El Hadri Hind[a,b], Lespes Gaëtane[a], Chéry Philippe [b], Potin-Gautier Martine[a]

[a]Université de Pau et des Pays de l'Adour/CNRS, LCABIE UMR5254, IPREM 2 avenue Pierre Angot 64053 PAU Cedex 09, France
[b] ENITA de Bordeaux, 1 cours du Général De Gaulle, 33175 Gradignan, France

hind.el-hadri@etud.univ-pau.fr

Since the XIX century, a copper based-fungicide has been systematically used in vineyard to fight against downy mildew, a plant pathogenic fungus. This treatment has led to increase the total copper concentration in soil due to its strong immobilisation by soil constituents. However, copper is also susceptible to be transferred to soil solutions and surface waters notably by colloidal transport. Indeed, the colloidal fraction is recognised as playing a key role in biogeochemical cycles of the trace elements (McCarthy, 1989). Particularly, it contributes to copper diffuse pollution, leading to a potential risk for water quality and aquatic organisms. Consequently, the characterization of colloidal phase in natural systems represents an important environmental as well as analytical challenge regarding the variety in shape, size and dispersion mechanism of nanoparticles originating from soils.

In this study colloidal fraction from drain waters sampled in a wine-growing soil were characterised and colloidal copper distribution determined by on-line Asymmetrical Flow Field Fractionation (As-Fl-FFF) hyphenated to several complementary detectors like Ultra-Violet (UV), light scattering (LS) and atomic mass spectrometry (ICPMS).

The results obtained confirm the relevance of such investigation strategy to assess the colloidal copper forms in the size continuum and thus better understand the fate of this element. Indeed, several colloidal populations with different nature and size are present in the media monitored. Copper appears linked to the organic populations, which are also showed to have specific mobility, leading to facilitated mobilisation of copper from soil to water. Additionally, considering the results the other soil constituents (such as Mn and Fe oxy-hydroxides) also appear to play a role in the mobilisation and the transport of copper.

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RD8

DOM-AFFECTED TRANSFORMATION OF CONTAMINANTS ON MINERAL SURFACES

Polubesova T. * and Chefetz B.

Department of Soil and Water Sciences, Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, P.O. Box 12, Rehovot 76100, Israel.

polubeso@agri.huji.ac.il

The transformation of organic and inorganic contaminants by mineral surfaces significantly affects their environmental behavior. Transformations such as redox reactions and hydrolysis of organic and inorganic contaminants on clay surfaces have been widely studied. However, the effects of dissolved organic matter (DOM) on these reactions and transformations by mineral surfaces have not been extensively explored and reviewed. This review analyzes the role of DOM in oxidation, reduction, hydrolysis and photochemical reactions of contaminants occurring on mineral surfaces. DOM impact on the transformation of contaminants by minerals manifests in three major processes: (i) competition of DOM for surface-active sites on the mineral surface; (ii) dissolution of minerals and exposing new surface sites on the mineral surface; and (iii) electron shuttling. Most of the data suggest that DOM reduces oxidation and hydrolysis, and increases reduction of contaminants by minerals. Alternatively, mineral surfaces can enhance redox transformations of contaminants due to interactions with DOM. DOM can serve as an electron-shuttling agent and thus increase reduction of contaminants due to the enhanced formation of surface-complexed Fe(II). Reduced species of DOM or strongly adsorbed low-molecular weight DOM containing aromatic components are responsible for this mechanism. DOM impact on transformation of contaminants varies as a function of its molecular composition and chemical properties. In some cases, low- and high-molecular-size DOM components exhibited opposite influences on the transformation of contaminants by minerals. In addition, adsorption and fractionation of DOM on the mineral surface can also influence the contaminant-mineral interactions. DOM can also affect the photochemical transformation of contaminants on mineral surfaces. DOM may play a dual role in the photochemical degradation of contaminants by minerals: the adsorbed DOM can act as a scavenger of VB holes, thus decreasing the oxidative mechanism of minerals surface; alternatively, scavenging of VB holes by electron-rich adsorbed DOM results in stabilizing electrons photo-promoted in CB and facilitating charge transfer reactions and reduction of contaminants.

Based on the reviewed data, we conclude that the evaluation of DOM effects on contaminant transformations in the DOM-mineral system needs to be based on the molecular-level structure and properties of the DOM and its structural fractions. A clarification of the effects of the DOM fractions, which differ in molecular weight, molecular structure, hydrophobicity and other properties, will advance our understanding of the mechanism of contaminant transformation in a DOM-mineral system. In addition, we suggest that “natural DOM” should be used to elucidate DOM impact on the mineral surface reactions and not dissolved commercial humic acids which exhibit quite different chemical structure and properties. A comprehensive study of DOM impact on the transformation of contaminants on mineral surfaces is needed to elucidate contaminant environmental behavior and to develop better remediation technologies.

RD9

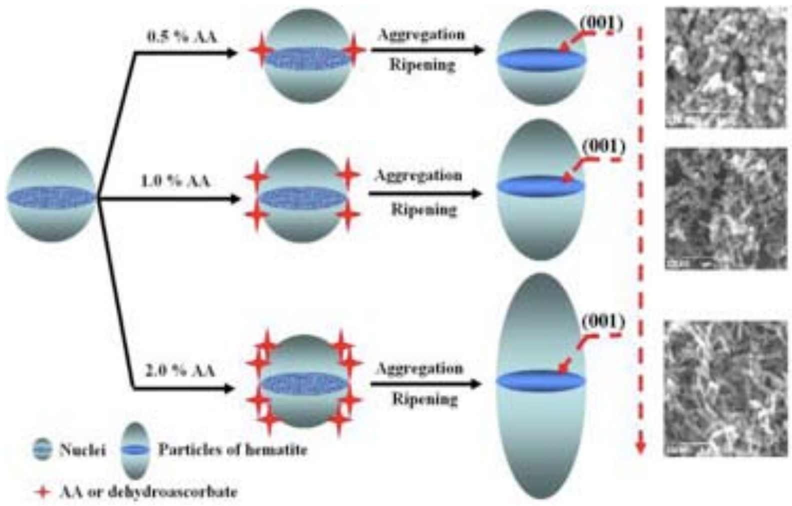
SHAPE EVOLUTION SYNTHESIS OF α-FE$_2$O$_3$ NANOPARTICLES BY ASCORBIC ACID AND THEIR CATALYZED DEGRADATION OF METHYLENE BLUE

Tan Wenfeng*[a,b], Yu Yating[a], Wang Mingxia[a], Liu Fan[a], Koopal Luuk K.[a,c]

[a] College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, P. R. China.
[b] State Key Laboratory of Soil Erosion and Dryland Farming on Loess Plateau, Institute of Soil and Water Conservation, Chinese Academy of Sciences, Yangling, Shanxi 712100,P. R. China.
[c] Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, the Netherlands

wenfeng.tan@hotmail.com

Iron oxides and hydroxides are widely present in nature and nano-particles of iron minerals are distributed throughout the atmosphere, oceans, groundwater, surface waters, soils, in and/or on most living organisms. In this paper the method is modified by using ascorbic acid instead of Fe(II). Ascorbic acidcan catalyze the reduction of Fe(III), already present in the reaction mixture, to Fe(II). The conditions under which ascorbic acidstrongly catalyzes the hematite preparation turn out to be a molar ratio ascorbic acid/Fe(III) of 0.5 to 2%. The molar ratio determines the morphology, which ranges from nearly spherical particles with a smooth surface to spindle type particles with a rough surface. The specific surface area of the spherical and ellipsoidal particles is very similar but that of the spindle type particle is substantially larger. The catalytic activity of the synthesized particles is tested by the enhanced degradation of methylene blue in solution. The α-Fe$_2$O$_3$ samples catalyze the degradation of methylene blue in the order spindles >>spheres > ellipsoids.



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PD1

IMPACT OF GENOME ON AGGREGATION AND ELECTROKINETICS OF MS2 PHAGE, INFLUENCE OF THE VIRUS PURIFICATION PROTOCOL

Dika C., Duval J. F. L.*, Merlin C. and Gantzer C.*

* C. Gantzer: Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), Université de Lorraine, CNRS, 5 Rue Albert Lebrun, F-54250 Nancy, France
J. F. L. Duval*: Laboratoire Environnement et Minéralurgie (LEM), Université de Lorraine, CNRS, 15 Avenue du Charmois, 54501 Vandoeuvre-Les-Nancy, France.

Christophe.Gantzer@pharma.uhp-nancy.fr - Jerome.Duval@ensg.inpl-nancy.fr

Outside their host cells, viruses are inert particles. Therefore, the dissemination and fate of viruses in aquatic media or their removal by water treatment process is mainly defined by their surface properties. In the specific context of water treatment, the F-specific RNA phage MS2 is classically proposed as a surrogate to evaluate the performance of pathogenic virus removals following various protocols, e.g. sand filtration, membrane or coagulation/flocculation. This phage is a soft (*i.e.* permeable) particle that consists of three concentric layers that differ in composition: a bulk RNA region, a RNA protein-bound layer, and a proteic capsid forming the outer shell of the virus. Recent studies have established that the electrokinetic properties of this phage were consistent with those predicted for soft, multilayered particles (Langlet *et al.*, 2008). Accordingly, it was evidenced that internal structure of viruses affects their interfacial properties and thus their propensity to aggregate.

Our investigation of electrokinetic and aggregation properties of MS2 phages as a function of pH and ionic strength and those of their corresponding VLPs (capsid without genome) confirmed the significant impact of viral genome (Dika *et al*., 2011). In particular, we observed a major difference between the ionic-strength dependence of electrophoretic mobilities for MS2 and corresponding VLPs, which reflects their different electrostatic and flow permeability properties in line with the theory developed by Langlet *et al*. (2008). In addition, there is a significant aggregation of MS2 viruses at pH values corresponding to their isoelectric point and lower (pH < 3.9), and no aggregation is detected for pH > 4 regardless the salt concentration. For VLPs, the situation is significantly different. VLPs aggregation is indeed only observed at their isoelectric point (pH = 3.5) and under low ionic strength conditions while stable VLPs suspensions are obtained under high-electrolyte concentration (100 mM $NaNO_3$). The recent analysis by Nguyen *et al.* (2011) does not confirm these observations but a different method of virus purification and VLPs synthesis was adopted. The impact of purification methods on viral surface properties then becomes a matter of concern and as such should deserve closer investigation. We therefore compared the electrokinetic and aggregation features of MS2 and VLPs purified according to three different protocols (dialysis, cesium chloride gradient associate with dialysis and PEG method). As expected, results showed that the adopted purification method significantly impacts the occurrence or not of virus aggregation since higher purification of MS2 phages result in the absence of aggregation at lower pH. Nevertheless, a major difference remains between the electrokinetic properties of MS2 and corresponding VLP as measured as a function of salt concentration. This means that VLPs may not be suitable model systems for predicting behavior of pathogenic viruses, mainly because of the significant impact of the internal genome on the overall physicochemical properties of viruses.

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PD2

INVESTIGATION OF TOPSOIL WATER DISPERSIBLE COLLOIDS (WDC) RELEASE KINETICS IN BATCH EXPERIMENTS

Jiang C.*, Séquaris J.-M., Vereecken H. and Klumpp E.

[1]Agrosphere, IBG 3, Forschungszentrum Jülich GmbH, D-52425 Jülich, German

c.jiang@fz-juelich.de

The release and stability of water-dispersible colloids (WDC) during soil erosion are factors affecting soil organic carbon and contaminants sequestration. We have investigated, in batch experiments, the release kinetics of water dispersible colloids (WDC) in three German topsoils from the network of terrestrial observatories (TERENO). The potential WDC releases along different shaking times, in distilled water, were compared in a temperature range from 7°C to 35°C. The mass of released WDC from topsoils increases along the series Wüstebach (forest soil) ≤ Rollesbroich (grassland soil) < Selhausen (arable soil) while the organic carbon (OC) content decreases along the same series. The surface properties of WDC were analyzed by N_2-adsorption (BET method) and their dispersion and stability behaviors in Na- and Ca-systems were characterized by critical coagulation concentrations (CCC) of Ca^{2+} and Na^{+}. It can be shown that the WDC mobilization was limited by a diffusion controlled step during the steady water flow conditions of batch experiments. The net interaction energy potential between WDC is not the limiting step for WDC release under the low ionic strength conditions of the batch experiments. WDC diffusion through immobile water layer of variable thickness at soil aggregates surface may explain difference between mobilization extents in the three topsoils, which was supported by the variations of specific surface area and sedimentation volume of the topsoils.

PD3

Session D: Environmental colloids and interfaces: properties, structure, reactivity

ELECTROHYDRODYNAMICS OF MULTIRESPONSIVE CORE-SHELL POLYMER PARTICLES

Martin J.[1]*, Rotureau E.[1], Pinheiro J. P.[2] Farinha J. P. S.[3] and Duval J. F. L.[1]

[1] Laboratoire Environnement et Minéralurgie, Nancy-Université, CNRS UMR 7569, 15 Avenue du Charmois, B.P. 40,
54501 Vandoeuvre-lès-Nancy Cedex, France
[2] CMQE/IBB, Departamento de Química e Farmacia/Facultade de Ciêncas e Tecnologia, Universidade do Algarve,
Campus de Gambelas, 8005-139 Faro, Portugal
[3] Centro de Química-Física Molecular and IN-Institute of Nanosciences and Nanotechnology, Instituto Superior
Técnico, 1049-001 Lisboa, Portugal

jennifer.martin@univ-lorraine.fr

Results presented in this poster are part of a first year PhD thesis program “Dynamic speciation of metal cations at biotic and abiotic ligand interphases”. One of our objectives is to understand the processes underlying the dynamic binding of metals by microgel-type colloidal particles. For that purpose, we used as model system core-shell polymer nanoparticles synthesized with a ca. 42 nm radius poly (methyl methacrylate) glassy core and an anionic multiresponsive shell made of crosslinked poly (N-isopropyl acrylamide-*b*-acrylic acid) (p(N-AA)) or poly (N-isopropyl acrylamide b methacrylic acid) (p(MA-N)). These two types of particles exhibit identical total charge [1] but differ according to the distribution of polymer segments in their shell. In details, the p(MA-N) particles have negative charges confined preferentially in the vicinity of their core whereas charges of p(N-AA) particles are distributed in the outer periphery of the shell. Dynamic Light Scattering measurements collected for the aforementioned system comfort results recently published on the dependence of the particles size with varying pH, ionic strength and solution temperature [1]. Depending on these aqueous medium conditions, the swelling ratio of the particles is governed by a balance between electrostatic repulsion, hydrophilic/hydrophobic interactions taking place between neighboring charges or segments of the shell. This explains, for instance, the shift of the volume-phase transition temperature towards higher temperatures with increasing pH, *i.e*. increasing the degree of protonation of carboxylic groups. We also observe that particles size varies according to power-law with ionic strength, which is expected for ionic microgel type particles. Size measurements were completed by systematic electrokinetic analyses over a large range of pH, ionic strength and temperature values. In particular, the presence of an asymptotic plateau value at large ionic strength demonstrates the soft nature (permeable to ions and flow) of the particles. A set of data was collected for both particles p(N-AA) and p(MA-N) and noticeable differences in terms of electrohydrodynamic properties will be discussed. Thorough quantitative analysis of these data using formalism for electrohydrodynamics of soft heterogeneous particles [2] is currently in process. These analyses will furnish the key electrostatic properties of particles as a function of medium chemical composition and will help in understanding chemodynamics of metal/particle complexes under a large range of pH, temperature and ionic strength values.

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ANALYSIS OF COLLOID RETENTION IN CRYSTALLINE ROCK

Albarran N., Missana T.*, Alonso U., García-Gutierrez M., López T.

CIEMAT, Avda. Complutense 40, Madrid 28040 SPAIN

tiziana.missana@ciemat.es

The evaluation of the impact of colloids on contaminant transport is important in the frame of the performance assessment (PA) of a high level radioactive waste (HLRW) repository emplaced in crystalline rock because rock fractures represent preferential paths for colloid migration. However, colloids may undergo interactions with the rock surface and filtration during their transport. In HLRW repositories, colloids of different nature are expected: from the natural ones to those formed by the engineered barrier materials (iron oxides, compacted clay, cement, etc.,). Depending on their properties, these colloids may show different transport behaviour, resulting in a different impact on contaminant migration.

In this study, the transport behaviour of latex, gold and montmorillonite colloids in a fractured crystalline rock was compared using appropriate chemical conditions to guarantee colloid stability (alkaline pH and low ionic strength). The effects of water velocity, particle size and fracture aperture on colloid transport were studied. Results showed that colloid transport was affected by the water velocity, the particle size, fracture aperture and hydrodynamic dispersion. In particular, colloid filtration was strongly dependent on the water velocity. Figure 1 shows the colloid recovery obtained in all experiments performed with latex, gold and montmorillonite colloid as a function of residence time in the fracture. The increase of the residence time (lower velocities) increases drastically the retention of all colloids even when unfavourable electrostatic conditions are present (colloid and rock both negatively charged). However, at similar water velocity, the recovery of montmorillonite colloids was always higher than that observed for latex and gold colloids, indicating that the nature and morphology characteristics of colloids also play an important role in their transport behavior. Additionally, the analysis of the fracture, after transport experiments, indicated that granite surface defects and the microroughness favor the colloid attachment, as will be discussed in the paper.

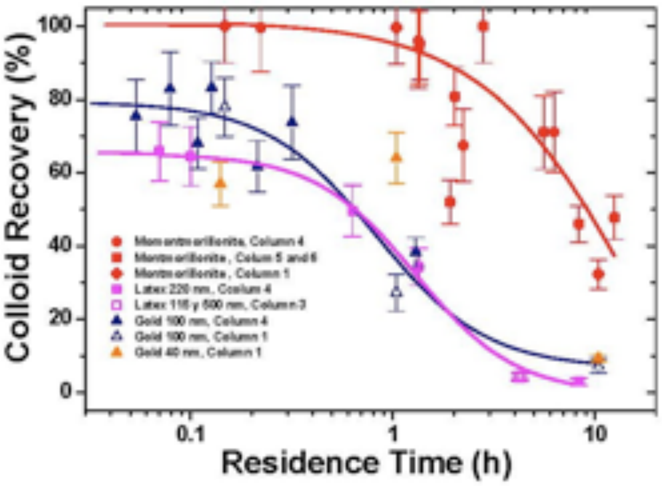

Figure 1. Recovery of latex, gold and montmorillonite as a function of the residence time in the fracture.

PD5

SORPTION OF METALS ONTO RIVER SUSPENDED MATERIALS

Vereecke J.[1], Montargès-Pelletier E.[1]*, Fraysse F.[1], Bauer A. [1], Rotureau E.[1], Ghanbaja J.[2], Salsi L.[1],
Wadwogel Y.[1], Gley R.[1], Razafitianamaharavo A.[1]

[1]Laboratoire Environnement et Minéralurgie, CNRS Université de Lorraine, 15 avenue du Charmois, BP 40, 54500 Vandoeuvre-les-Nancy, France
[2]SCMEM, Université de Lorraine, Boulevard des Aiguillettes, BP 239, 54506 Vandoeuvre-Lès-Nancy

emmanuelle.montarges@univ-lorraine.fr

In rivers, particles and colloids play a crucial role in the transport and fate of organic and metallic contaminants. The global composition of particles within aquatic suspensions is usually determined by analytical schemes including size fractionation, elemental analyses. However, it appears crucial to be able to establish a link between river material properties and their sorption capacities towards contaminants such as metals.
For that purpose, suspended material were collected in three different points along the Moselle river, before and after the junction with its main tributary, the Meurthe river, and after the junction with highly contaminated rivers from the downstream region of the Moselle watershed. Thanks to the use of field-centrifuge, several dozens of grams of matter could be sampled for each station, allowing a fine and detailed characterization of aquatic divided solids, as well as the study of metal sorption onto these natural aquatic particles (Cd, Zn and Pb).
Elemental composition, mineralogy of samples was examined through ICP-MS, XRD, FTIR spectroscopy, TEM combined with EDX spectroscopy. Supplementary analyses were perfomed before metals sorption experiments in order (i) to determine specific surface area and porosity, (ii) to reveal chemical status of inherent metals. Sorption isotherms of metals were carried out in batch conditions, at fixed solid/liquid ratio, ionic strength and pH, initial and final concentrations were measured through atomic absorption methods.
Suspended particulate matter (SPM) were collected under high flow conditions. The samples from the different stations were rather close in composition, displaying clay minerals as predominant mineral phases (illite, kaolinite, chlorite and interlayered illite/chlorite). Also, their contents in trace metals were similar, with a slight higher contamination level for the downstream station. SPM shown rather high affinity for the three metals, as between 90 and 98 % of metals were removed from solutions.

BIOFILM INSIDE ENVIRONMENT PREVENTING OUTSIDE POLLUTION

Morisaki H.[1]*, Tsuchiya Y.[1], Kuriniawan A.[1], Hiraki A.[2]

[1]Graduate School of Science and Engineering, Ritsumeikan University 1-1-1 Noji Higashi, Kusatsu, Shiga, 525-8577, Japan

[2]LS Product Development Dept. Product Development Div. 2, Sysmex Corporation 4-4-4 Takatsukadai, Nishi-ku, Kobe 651-2271, Japan

morisaki@sk.ritsumei.ac.jp

The nutrient ion concentrations in the interstitial water of biofilms (BFs) formed on reed and stone surfaces in a natural lake environments were investigated. The followings were found for both types of BF: 1) the concentrations of ammonium, nitrate, nitrite, and phosphate ions were much higher (ca. 400-fold for nitrate and nitrite to 2300-fold for phosphate) than those in the surrounding lake water; 2) the nutrient ion concentrations in the BFs changed seasonally in synchrony with the changes in the lake water as exemplified in Fig.1 for nitrate ion.

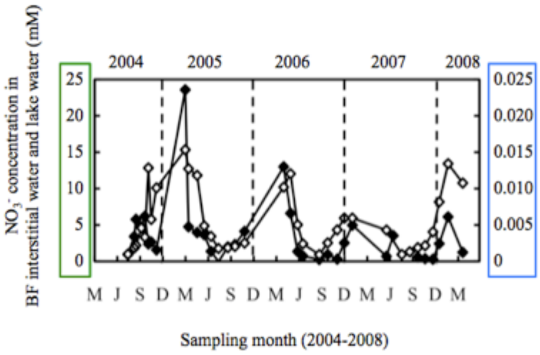

Fig. 1 Seasonal variation of concentrations of nitrate ion in the interstitial water of the BF on stone (solid symbol; see left-hand y-axis for the value) and in the nearby lake water (open symbol; see right-hand y-axis).

Measurements of electrophoretic mobilities of biofilm under various pHs revealed that BF-polymers carry both positive (due to amino-group) and negative (due to carboxylic group) electric charges. The electrostatic attractive interaction between these charges and oppositely charged ions outside BF seems to be a driving force to enrich nutrient ions inside BF. The enrichment of nutrient ions inside BF means removal of these ions from outside BF. Thus, this function of BF leads to suppress pollution outside BF, e.g., lake water, caused by increment in concentrations of nutrient ions. Dynamics of ion adsorption and desorption on the BF are now being investigated. The results will be discussed in the session.

PD7

COLLOID-CHEMICAL PROPERTIES OF COMPOSITIONS OF POLYACRILONITRILE DERIVATIVES WITH SURFACTANTS

Mutaliyeva B.Zh., Madybekova G.M., Aidarova S.B.

M.Auezov South-Kazakhstan State university, Shymkent, Moldagulova street, 8-a, 17, Kazakhstan

Mbota@list.ru

Amongst water-soluble polymers intended for work with various dispersed systems, the polyacrylonitrile derivatives have a special place. They possess a specific composition and structure, are polyelectrolytes, have universal properties. Thus and so they are broadly used in range of important industry branches, such as chemical, oil-producing, agrochemical industries.

In this paper the researches results about colloid-chemical properties of compositions on the base of polyacrylonitrile derivatives with surfactants are reduced with purpose of development of scientific-substantiated approach to their usage, especially for clearing of oil emulsions that have important practical importance along with theoretical.

From results of electrokinetic investigations have been obtained that in the field of relative concentration of Hydrolized Polyacrylonitrile (HPAN) $\beta = 1 \div 2,5$ the charge of complex are defined by sign of OlNa mycelles. Futher increase of HPAN concentration into solution bring to increasing of quantity of involved into electrostatic contacts their functional groups, whereof testify decreasing of ξ -potential of OlNa mycelles and its inversion at $\beta > 2,5$. In this condition the sign of complex charge are defined by HPAN charge sign. It should be noted that such importance of electrostatic interactions in case of titration Polyacrylamide (PAA) with OlNa solution are reached only at acidation of solution up to pH=4.

From investigations of dependences of electrostatic interactions degree between HPAN and OlNa, OlNa and PAA from their relative concentrations $\theta = f(\beta)$ have shown that it reach of high importances, at concentration correlations $\beta = 1$ the importance θ for system HPAN-OlNa reach up to 35 %, at further increasing of HPAN concentration the importance θ reach up to 65 %. This allow to conclude that between HPAN and OlNa, OlNa and PAA the nonstoichiometric complexes are formed because of electrostatic interations between polyelectrolyte and surfactant mycelles.

Thereby, research results allow to suppose that at relative concentration of polyelectrolytes in composition with surfactant $\beta=2,5$, are the most optimal for usage in such processes as oil demulsification, emulsion stabilization at obtainment of metalls nanoparticles etc.

PD8

STUDIES OF PROPYL GALLATE ANTIOXIDATIVE ACTIVITY IN THE N-OXIDE SURFACTANT SOLUTIONS

Szymula M.[1], Wilk K. A.[2], Sienkiewicz A.[1] and Narkiewicz-Michałek J.[1]*

[1] Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland
[2] Department of Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland

Jolanta.Narkiewicz-Michalek@umcs.lublin.pl

It is recognized that the reactive oxygen species (ROS) are implicated in all stages of lipid peroxidation (initiation, propagation, and termination). Depending of the nature of the lipid, these oxidative reactions could modify oil composition, cell membranes, or the integrity of lipoproteins. There is abundant evidence that polyphenols present in foods and beverages can inhibit lipid peroxidation processes acting as chain breaking antioxidants. The efficiency of a particular antioxidant is mainly determined by its reactivity towards ROS, the stoichiometry of the reaction, and its ability to reach lipid phases. Nowadays, there is observed increasing interest concerning the investigation of the antioxidant capacity of polyphenols such as gallic acid and its hydrophobic derivatives.

The activity of antioxidants in foods and biological systems is dependent on a multitude of factors, including the colloidal properties of the substrates and the localisation of antioxidants in different phases. One of the methods of testing antioxidants activity in vitro is investigation of their decomposition in surfactant solutions and microemulsions.

Among many types of surfactants, surface active N-oxides are an interesting subclass due to their simple methods of preparation, low or no-toxicity, good biodegrability and very effective performance. They are very useful in shampoos, hair conditioners, dish and laundry detergents, fabric softeners and the like. They may be also used as the carriers of bioactive substances, e.g. antioxidants such as vitamin C, propyl gallate and vitamin E. In this communication the results of propyl gallate atmospheric oxidation in the three new N-oxide surfactant solutions obtained by UVvis spectroscopy are presented.

As follows from our studies, in the solutions containing N-oxides propyl gallate undergoes slower oxidation reaction with atmospheric oxygen than in pure water and the rate of reaction decreases with the increasing surfactant concentration. This effect is reversed to that exerted by the same surfactants on vitamin C. It was observed that the presence of N-oxides destabilized vitamin C and the effect grew for higher surfactant concentration.

PD9

EFFECT OF AN APPLIED STRAIN CAUSED BY ALKALINE PERTURBATION ON THE CATIONIC EXCHANGE CAPACITY OF DIOCTAHEDRAL SMECTITE: QUANTITATIVE XRD INVESTIGATION.

Chalghaf R.[1], Oueslati W.[1,2]*, Ammar M.[1], Ben Rhaiem H.[1], Ben Haj Amara A.[1]

[1] UR05/13-01: Physique des Matériaux Lamellaires et Nano-Matériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia

[2]Faculté des sciences de Gafsa, Département de physique, campus universitaire Sidi-Ahmed Zarrouk 2112 Gafsa, Tunisia

walidoueslati@ymail.com

This work aims to determine the strain effect caused by an alkaline perturbation, obtained by after rapid equilibration (3 hours) under pH-controlled conditions (4-8 pH range)., on the cationic exchange process in the case of Na rich-montmorillonite (Swy-2) . This goal was accomplished in two steps. First to prepare and characterize a stressed final product who are used after that in the selective exchange study. In the second step, strained materials was considered like starting sample and used to verify the effect of the "materials history" on the selective exchange process studied by [1], CEC and surface area. The quantitative analysis of XRD patterns is achieved using an indirect method based on the comparison of experimental XRD patterns with calculated ones. This investigation allowed us to determine several structural parameters related to the nature, abundance, size, position and organization of exchangeable cation and water molecule in the interlamellar space along the c* axis.

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PD10

HYDRATION-DEHYDRATION PERFORMANCE OF (Na^+, Cs^+) EXCHANGED SMECTITE: EFFECT OF THE CHARGE LOCATION AND THE CATION NATURE

Ammar M.[1], Oueslati W.[1,2]*, Ben Rhaiem H.[1] and Ben Haj Amara A.[1]

[1] UR05/13-01 : Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH),
Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia
[2]Faculté des sciences de Gafsa, Département de physique, campus universitaire Sidi-Ahmed Zarrouk
2112 Gafsa, Tunisia

walidoueslati@ymail.com

This works aims at investigating the bonds between dehydration–hydration behaviors, charge location and the ionic radius in the case of dioctahedral smectites. For that, a natural
montmorillonite and beidellite with different charge location (respectively di and trioctahedral) was selected. The starting samples were exchanged in first time with Na^+ cation followed by a cesium (i.e.Cs^+) cationic exchange process.

The evolution of hydration behaviors was investigated by varying %RH condition. All exchanged samples were studied "insitu" using XRD analysis with her both qualitative and quantitative analyses. This method allowed us to characterize the evolution of structural's parameters deduced from the proposed theoretical mixed layer structure (MLS) used to fit experimental XRD patterns.

Obtained results, in the case of Na^+ and/or Cs^+ exchangeable cations, show an increase of hydration heterogeneity degree in the case of dioctahedral smectite (beidellite) characterized by a relatively low number of Mixed Layers Structure. For the same sample, the Cs^+ exchange process induces a hydration homogeneity trend. This result was interpreted by a new interlamellar space organization along c* axis which are confirmed by studying the evolution of relative abundances related respectively to dehydrated 0W, monohydrated 1W, bihydrated 2W layers along the hydration-dehydration process.

PD11

DEGRADATION OF GLYPHOSATE AND AMPA (AMINO METHYL PHOSPHONIC ACID) SOLUTIONS BY THIN FILMS OF BIRNESSITE ELECTRODEPOSITED.

Ndjeri M.[1], Pensel A.[1], Peulon S.[1]*, Haldys V.[1], Chaussé A.[1]

[1] CNRS - Université d'Evry - CEA, « Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement », UMR 8587, Boulevard François Mitterrand, 91025 Evry, France

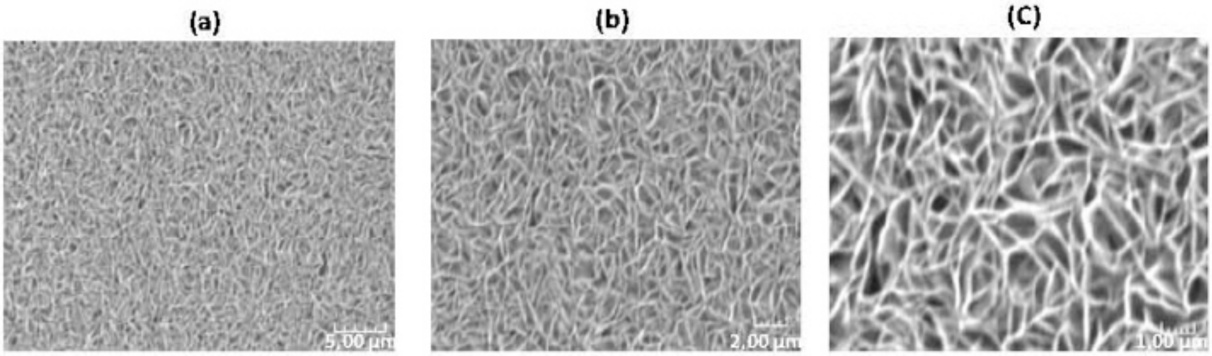
sophie.peulon@univ-evry.fr

Glyphosate is one of a pesticide the most used in the world. AMPA (amino-methylphosphonic acid) is the principle metabolite of glyphosate more toxic and more persistent than glyphosate. These two compounds are the most found in waters in environment as pollutants, that is why it seems very important to found a simple method to eliminate these two main pollutants present in surface and groundwaters.

Previously, we have shown that thin films of birnessite, electrodeposited onto a cheap transparent semiconductor substrate (SnO_2), can significantly degrade and mineralise organic dyes [1,2] due to the spontaneous oxidant properties of birnessite, which is the major manganese compound present naturally in the environment.

We report also the successful use of thin films of birnessite to study and to remediate aqueous solutions containing glyphosate and AMPA. We have shown that glyphosate is degraded, with simultaneous formation of AMPA, formaldehyde, phosphate ion, nitrate ion and ammonium ion, without macroscopic modification of birnessite. The last four by-products are also obtained during the degradation of AMPA by birnessite.

Various experimental parameters such concentration of pollutant, temperature, agitation, presence or not of dioxygen were studied and mechanisms were proposed. The good yields obtained during glyphosate/birnessite and AMPA/birnessite interactions without any energy supply permit to envisage a possible application of these thin films for the treatment of wastewater.



SEM pictures of birnessite thin films electrodeposited onto SnO_2 (a) X 1000, (b) X 5000, (c) X 10000

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PD12

DYNAMIC SPECIATION ANALYSIS OF METAL BINDING BY HETEROGENEOUS PARTICLES: CASE OF CLAY MINERALS

Rotureau Elise

Laboratoire Environnement et Minéralurgie, Nancy-Université, CNRS UMR 7569, 15 Avenue
du Charmois, B.P. 40, 54501 Vandoeuvre-lès-Nancy Cedex, France

elise.rotureau@univ-lorraine.fr

Reactive transfer of metal ions in fresh water is mainly controlled by chemical and physical processes occurring at interfaces of finely divided matter. These solid phases are generally heterogeneous in terms of size, shape, nature and density of charges (or binding sites). To our knowledge, little attention is paid to understand the impact of particle heterogeneities on dynamic aspects of metal ions speciation (mass transport and kinetics properties) [1–3]. Among the analytical techniques for speciation analysis, stripping chronopotentiometry at scanned deposition potential (SSCP) is a useful tool for examining the thermodynamics and kinetic features of metal complexes. SSCP involves a first step of metal deposition at a rotating disk electrode coated with a mercury film (accumulation step) and a second step of metal redissolution *(i.e.* reoxydation), allowing the quantification of the total accumulated metal. SSCP waves are then constructed from the reoxydation transition time versus the deposition potential. A quantitative approach provides rich information on the kinetic of the association/dissociation of metal complex coupled with the mass transport of the overall metal species, as well as heterogeneous complexation parameters. In addition, stripping technique of AGNES (Absence of gradients and Nernstian equilibrium stripping) is used for the direct determination of the free metal concentration which gives complementary and helpful data for SSCP interpretation [4]. In this work, we examined the metal complex formation with size-fractionated clay samples (Wyoming montmorillonite) [5]. These mineral phases are known to have a permanent negative structural charge on the basal faces and ampholitic edge hydroxyl groups. Three size samples were tested in presence of metallic ions (Pb, Cd). Comparison of SSCP waves for each metal suggests that lead complexation is much more heterogeneous and stronger than that of cadmium. Cd-Wy complexes are SSCP-labile in a large range of pH suggesting a weak electrostatic type of binding. In contrast, we observed a lability loss of the Pb-Wy complexes with the increasing of pH, evidencing the formation of inner-sphere surface complexes. By varying the rotating speed of the disk electrode, effect of the hydrodynamic conditions (convection/diffusion) is also examined. Preliminary results indicate a change of the global dynamic response with the increasing of the rotation speed. Since SSCP shape is, in this case, a double indicator of metal binding heterogeneity and lability loss of the system, additional analyses are currently performed to clarify the chemodynamics of metal-clays complexes.

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PD13

STRUCTURAL-ADSORPTION CHARACTERISTICS OF SBA-15 ORGANOSILICAS FUNCTIONALIZED WITH DIFFERENT GROUPS

Barczak M.[1]*, Rudziński W.[1], Borowski P.[1], Zięba E.[2]

[1] Faculty of Chemistry, Maria Curie-Sklodowska University,
Maria Curie-Sklodowska Sq. 3, 20 031 Lublin, POLAND
[2] Zoology and Ecology Department, SEM Laboratory, Catholic University of Lublin,
Krasnicka St. 102, 20-718 Lublin, POLAND

mbarczak@poczta.umcs.lublin.pl

Ordered mesoporous organosilicas are very attractive materials due to their high surface areas, large volumes of ordered mesopores and diverse morphology what makes them attractive potential catalysts and adsorbents [1-6]. From the other hand the possibility of introduction of the organic groups into the ordered structure of the final material during the synthesis is an invaluable advantage of the sol-gel processing of organosilicas [7-9]. In the present work channel-like mesoporous organosilicas (SBA-15) were synthesized via co-condensation of tetraethyl orthosilicate (TEOS) with alkoxysilanes bearing terminal amine-, thiol-, vinyl-, phenyl- and cyano- groups in the presence of Pluronic P123 triblock copolymer.

Obtained SBA-15 materials were characterized by infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy and nitrogen sorption measurements. The resulted materials exhibit well-ordered mesoporous structure, high values of specific surface areas and pore volumes and a high content of functional groups introduced by co-condensation. The sizes of ordered mesopores are in the range of 6-10 nm. It was establish that even small amount of alkoxysilanes substantially changes the properties of the final materials so co-condensation can be used not only to introduce the surface functional groups but also to modify the structural-adsorption characteristics of the resulted materials.

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PD14

ELECTROCHEMICAL STUDIES OF ALKYL GALLATES BEHAVIOUR IN SDS/WATER/ETOH SOLUTIONS

Sienkiewicz A., Szymula M.*, Narkiewicz-Michałek J.

Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, 20-031, Poland

szymula@hektor.umcs.lublin.pl

Gallic acid and its esters are synthetic antioxiodants used to protect food and other products against oxidation. Their electron-donating ability depends on their chemical structure and properties of the medium they are supposed to protect and can be quantitatively assessed on the basis of the electrochemical characteristics. In the presentation the results of electrochemical oxidation of two gallic esters: propyl gallate (PG) and lauryl gallate (LG) in various SDS solutions using the cyclic voltammetry method (CV) with a glassy carbon electrode will be shown. The dependences of peak current and peak potential on the surfactant concentration were determined in the water and the water+ethanol (EtOH) mixture, pH=2, 4, 11.

On the basis of the obtained results the effects of pH, surfactant and ethanol on the oxidation reaction kinetics were discussed. The most pronounced effect on the oxidation parameters of both gallates is due to pH changes; the lower pH, the higher value of oxidation potential. It means that the oxidation is more difficult under acidic conditions.

For PG the noticeable increase of peak potential and the decrease of peak current with the increasing surfactant concentration were observed up to the CMC. Beyond the CMC, the values of these parameters became almost constant. The addition of EtOH had only a small effect on the PG oxidation parameters and reduced that of the SDS concentration.

The more hydrophobic derivative LG is water insoluble and was investigated only in the aqueous systems containing high concentrations of SDS (solubilisation in micelles) and in the mixed H_2O+EtOH solvent containing SDS. Here the changes of oxidation parameters with the increasing surfactant concentration were much less pronounced than those for PG, but still the oxidation process was more difficult at lower pH values.

PD15

RHEOLOGICAL BEHAVIOR OF IMOGOLITE SUSPENSIONS

Yoshida A., Tsujimoto Y.*, Kobayashi M., Adachi Y.

Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennoudai,
Tsukuba, Ibaraki 305-8572, Japan

s1130246@u.tsukuba.ac.jp

Imogolite is one of the most important clay mineral contained in volcanic ash soil and is used as a natural coagulant. The morphology of imogolite is very unique with thin fibrous tube, whose inside and outside diameters are approximately 1 nm and 2 nm, respectively. The chemical structure demonstrates that the SiOH groups are located along inner wall of tube and the AlOH groups exist on the outer surface of the tube. Because of this morphology and chemical structure, imogolite coagulates under high pH. In the present study, we focus on the difference of rheological behavior of the imogolite suspension between that at dispersed state (pH4) and coagulated state (pH9). Experiments were carried out using a concentric cylindrical viscometer as a function of volume fraction. Applied shear rate increased from 6.45 s^{-1} to 258 s^{-1} and then decreased to the initial value. This procedure was repeated for three times. The flow curves for imogolite suspensions at pH 4 showed slightly hysteresis (Fig.1). During successive shearing cycles, the viscosity of imogolite suspension increased as shearing cycles increased. Additionally, shear thinning, a decrease of the viscosity with increasing shear rate emerged. We considered the shear thinning is due to the alignment of the imogolite. On one hand, at pH 9, the area of hysteresis loop became larger with increasing volume fraction (Fig.2). The flow curves tended to be constant as shearing cycle increased. The appearance of the yield stress was revealed from the intercept of the flow curve. Moreover, shear thinning at high pH was more remarkable than that at low pH. These obtained results indicates the condition of high pH for imogolite suspensions induces coagulation and non-Newtonian behavior. We consider that imogolite flocs are repeatedly subjected to breakup and coagulation by the given shear stress and thus the stronger structure is formed.

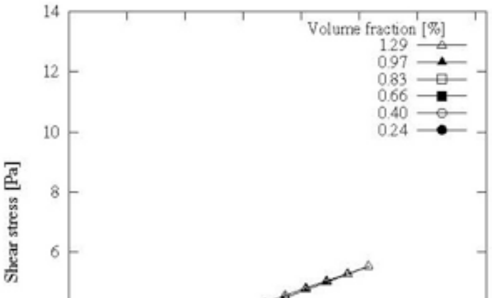

Fig.1 The flow curve of imogolite suspensions at pH 4

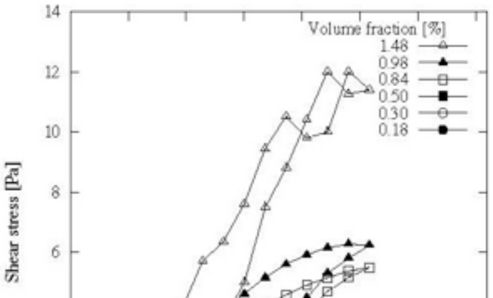

Fig.2 The flow curve at pH 9