IV INTERNATIONAL CONFERENCE INTERFACES AGAINST POLLUTION Granada, Spain June 4-7 2006

IAP 2006



IV INTERNATIONAL CONFERENCE Interfaces Against Pollution

BOOK OF ABSTRACTS

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Welcome

This is the fourth edition of the Interfaces Against Pollution Conferences. We acknowledge the honour of having our city chosen as venue for it, and it is our most sincere wish that this edition will be as successful as the previous ones, that you enjoy our city, and that the Conference will maintain its position in the difficult and overcrowded family of scientific events all around the world.

Fortunately, and thanks to the enthusiasm of a number of people, including the members of the present and previous Advisory Committees, the IAP meetings never stopped gaining interest from the colloid-science community, reflecting in fact the equally growing involvement of all social spheres in environmental protection and remediation. There has been a deep understanding that the world of colloids and interfaces has much to say in these matters. Such phenomena as the behavior of soils, humics and other natural colloids, the colloidal stability in aqueous media, adsorption and adhesion, transport processes, etc., have progressively found applications in the environmental investigation. That these remain mixed fields is demonstrated by the variety of contributions that we have received, ranging from the very chemistry of natural interfaces to theoretical models on the behavior of soft particles, or of concentrated suspensions, to mention just a few.

We have tried to fix a program that fits in all these research interests while keeping the duration of the conference relatively short, and avoiding the simultaneous running of various sessions. We apologize those of you that have seen their oral proposals converted into posters, and thank you for your understanding.

We thank you all for your attendance to the Conference, and wish you a pleasant stay in Granada, and the highest scientific success in this and future editions.

Fernando González-Caballero and Ángel V. Delgado Granada, June 2006

	Sunday, June 4	Monday, June 5	Tuesday,	Wednesday,
8.20-9.00	June 4	(Chair: W.H. Van Riemsdijk)	(Chair: L.K. Koopal)	(Chair: R. Kretzschmar)
		PL2. J. Puy	PL4. M. Elimelech	PL6. W. Van
9.00-9.20		O5. R. Kookana	O21. M. Auffan	O37. A.Altin
9.20-9.40		O6. M. dos Santos- Alfonso	O22. M. Barczak	O38. F.G. Fermoso
9.40-10.00		O7. M. Borisover	O23. J. Labille	O39. R Barna
10.00-10.20		O8. C. Galindo	O24. F.A. Weber	O40. J. F. Gálvez
10.20-10.40		O9. S.M. King	O25. D.C. Gooddy	O41. W. Rudzinski
10.40-11.00		Break	Break	Break
11.00-11.20		(Chair: M. Elimelech) O10. E. Tombácz	(Chair: H. Ohshima) O26. K. Laszlo	(Chair: E.R. Graber) O42. I. Alfred
11.20-11.40		O11. N. Takisawa	O27. K.L. Chen	O43 R.J. Crawford
11.40-12.00		O12. S. Friedman	O28. S. Klitzke	O44. M. Lenz
12.00-12.20		O13. K. Malysa	O29. E. Klumpp	O45. M. Evangelou
12.20-12.40		O14. Y. Adachi	O30. H. Chen	
13.00-15.00		Lunch	Lunch	Lunch
15.00-15.40	REGISTRATION	(Chair: S.B. Aidarova) PL3. H. Ohshima	(Chair: J. Gregory) PL5. N. Mishchuk	(Chair: N. Mishchuk) PL7. R. Kretzschmar
15.40-16.00	REGIOTRATION	O15. T.D. Waite	031. J. Rose	O46. V. Zakharenko
16.00-16.20		016. P. Behra	032. H. Sakaguchi	O47. J.C. F. Toledano
16.20-16.40		017. J. Gregory	U33. B. Kornilovich	048. N. Carrasco
16.40-17.00		Break	Break POSTER SESSION BEGINS	Farewell coffee
17.00-17.20	Official opening	(Chair: Y. Adachi) O18. S.B. Aidarova	(Chair: E. Tombácz) O34. D.E. Akretche	End of the Conference
17.20-17.40	(Chair:	O19. N. Kallay	O35. M.A. Blesa	
17.40-18.00	PL1. L.K. Koopal	O20. E. Guillon	O36. S. Tomlinson	
18.00-18.20	O1. S. Stoll			
18.20-18.40	O2. E.R. Graber			
18.40-19.00	O3. G.E. Morris		DOSTED	
19.00-19.20	O4. G. Schaumann		SESSION conf'd	
	15.00-19.00: Registration desk open	8.20-11.00: Registration desk open		
NOTES	21.00 Welcome party. Carmen de los Mártires (Buses: Conference Center)	21.00 Conference dinner. Restaurant "La Chumbera" (Buses: Conference Center)	21.00 Buses depart for the <i>Alhambra</i> visit (Conference Center)	

PROGRAM

CONTRIBUTORS

PL1	Ion binding to humics and minerals.
ס זם	L.K. Koopal, Wageningen University, The Netherlands.
PL2	I Duy University of Lloide Spain
PI 3	J. 1 uy, University of Lieua, Spann Electrokinetics of particles with complex surfaces
1 110	H Obshima University of Tokio Japan
PL4	Microbial Adhesion and Transport in Aquatic Environments
	M. Elimelech, Yale University, New Haven, USA.
PL5	Fundamental problems of soil decontamination by application of an
	electric field.
	N. Mishchuk, Institute of Colloid Chemistry and Water Chemistry,
	National Academy of Sciences of Ukraine, Kiev.
PL6	Binding of variable charge colloids, like humics to charged mineral
	surfaces, and its effect on ion adsorption.
	<u>W. Van Riemsdijk</u> , L.P. Weng, Wageningen University, The
	Netherlands.
PL7	Interactions between organic acids and siderophores at the oxide-water
	interface.
	R. Kretzschmar, P.U. Reichard, S.W. Frazier, S.M. Kraemer, ETH
01	Zürich, Switzerland.
01	Polyelectrolyte adsorption at colloid surfaces. Monte Carlo simulations
	S Stell A Laguagin S Illigh M Saija University of Canava
	<u>5. 51011</u> , A. Lagueen, S. Offich, M. Seijo. Officeisity of Geneva, Switzerland
02	Neither "adsorption" nor "partitioning": a link disruption model for
04	organic compound-soil organic matter interactions
	E.B. Graber, M. Borisover, Institute of Soil, Water and Environmental
	Sciences. Bet Dagan. Israel.
O3	Smectite suspension structural behaviour.
	G.E. Morris, M. Zbik, D. Elsby. University of South Australia.
04	Do biofilms affect the water repellency of urban soil samples?.
	G.E. Schaumann, B. Braun, D. Kirchner, E. Grohmann. TU Berlin,
	Germany.
O5	Nature and interactions of black carbon surface with organic
	contaminants and implications for environmental risks.
~ ~	R. Kookana, CSIRO Land and Water, Glen Osmond, Australia.
06	Picloram adsorption on clays.
	J.L. Marco Brown, R.M. Torres Sanchez [*] , <u>M. dos Santos Alfonso</u> .
07	University of Buenos Aires and "CETMIC, Argentina.
07	interactions of organic compounds in hydrated and non-hydrated
	M Borisover I Lapides* S Variy* II Milcongrin Z Corstl F
	Burshtein Institute of Soil Water and Environmental Sciences and
	*The Hebrew University of Jerusalem Israel
08	Study of the stability of concentrated acueous clay/magnetite
	suspensions.
	C. Galindo-González, G.R. Iglesias, F. González-Caballero, J.D.G.
	Durán. University of Granada, Spain.

O9	SANS studies of natural aquatic colloids.
	S.M. King, H.P. Jarvie [*] , ISIS facility, Rutherford Appleton
	Laboratory, Chilton, Didcot, and *Centre for Ecology and Hydrology,
010	Wallingford, U.K.
010	Particle network formation in soils: is there aggregating or dispersing
	effect of numic substances?. E. Tombéer, A. Mairily, Za, Cribulua, K. Kowées, University of Sporad
	E. TOMDACZ, A. MAJZIK, ZS. OZIDUIYA, K. KOVACS, UNIVERSITY OF SZEGEG,
011	nungary. Evaluation of amphiphilia properties of fulvia acid and humic acid by
011	allydpyridinium binding study
	M M Voe T Miyajima N Takisawa Saga University Japan
012	A new method to characterize interactions between counter ions and
012	charged particles via Wien effect measurements in dilute suspensions
	S. Friedman, C.B. Li [*] . Institute of Soil. Water and Environmental
	Sciences, Bet Dagan, Israel, and Institute of Soil Science, Nanjing,
	China.
O13	Velocity of rising bubbles as a method of detection of organic
	contaminations in water.
	J. Zawala, K. Swiech [*] , K. Malysa, Institute of Surface Chemistry
	PAS, and *Jagiellonian University, Cracow, Poland.
014	Rheological properties of dilute suspensions of montmorillonite.
	<u>Y. Adachi</u> , S. Kobayashi, N. Sakairi, Tsukuba University, Japan.
015	Factors influencing the rates of formation and dissolution of
	amorphous iron oxides in aquatic environments.
016	1.D. Waite, The University of New South Wales, Sydney, Australia.
010	Influence of pH buffer organic metter and initial mercury
	concentration
	V Wernert* F H Frimmel** P Behra ENSIACET Toulouse
	France, *Université Louis Pasteur, Strasbourg, France, and
	**Universität Karlsruhe, Gernany.
017	Formation and breakage of hydrous ferric oxide aggregates.
	J. Gregory, University College London, U.K.
018	Foam stabilization by compositions of surfactants with sodium
	carboxymethylcellulose.
	S.B. Aidarova, Zh.B. Ospanova, K.B. Musabekov, Kazakh-British
010	Technical University, Almaty, Kazakhstan.
019	Surface potential at metal oxide aqueous interface in the presence of
	organic adsorbents.
∩ 20	<u>N. Kallay</u> , 1. Freecalli, University of Zagreb, Croatia.
020	spectroscopic studies
	S Boudesocque E Guillon M Aplincourt GRECI UFR Sciences
	Reims. France.
021	Maghemite nanoparticles: an effective adsorbent for arsenic removal.
	M. Auffan ¹ , R. Jerome ¹ , J.L. Hazemann ² , M. Armand ¹ , J.P. Jolivet ³ ,
	J.Y. Bottero ¹ , ¹ Université Paul Cézanne, aix en Provence, ² Laboratoire
	de Cristallographie, CNRS UPR 5031, Grenoble, and ³ Laboratoire
	Chimie de la Matière Condensée, CNRS/UPMC, Paris, France.

O22 Functionalized bridged polysilsesquioxanes as adsorbents of volatile organic compounds. A. Dabrowski, M. Barczak, Yu L. Zub*, Marie Curie-Skłodowska University, Lublin, Poland, and *Institute of Surface Chemistry, NAS of Ukraine, Kiev. Transport and fate of carbon nanoparticles C60 in aquatic, soil, and **O23** organic environments. <u>J. Labille</u>, J. Brant^{*}, M. Wiesner^{*}, J.Y. Bottero, CEREGE, University of Aix-Marseille II, Aix en province, France, and *Rice University, Houston, USA. **O24** Colloid-facilitated transport of pollutants under variable redox conditions in a temporary flooded riparian wetland soil – A Microcosm Study. F.A. Weber, A. Voegelin, R. Kretzschmar, ETH Zürich, Switzerland. O25 Colloidal transport of pesticides in UK aquifers. D.C. Gooddy, D.J. Lapworth, I. Harrison, A.W. Kim, British Geological Survey, Nottingham, U.K. O26 pH-dependent adsorption and desorption of phenol and aniline. K. Laszlo, E. Tombacz^{*}, Cs. Novak, Budapest University of Technology and Economics, and *Szeged University. 027 Aggregation and deposition kinetics of fullerene nanoparticles in aquatic environments. K.L. Chen, M. Elimelech, Yale University, New Haven, USA. **O28** Cation bridging of colloids as indicated by multi-stage tangential ultrafiltration. S._Klitzke, J. Kirby*, E. Lombi*, R. Hamon*, F. Lang, Berlin University of Technology, and *CSIRO Land and water, Glen Osmond, Australia. **O29** Transport of metabolically active microorganisms in unsaturated porous media. E. Klumpp, G. Gargiulo, P. Ustohal, S. Bradford^{*}, J. Simunek^{*}, N. Tufenkji^{**}, H. Vereecken, Agrosphere Institute, Jülich, Germany, *George E. Brown Jr. Salinity Lab., USDA, Riverside, USA, **McGill University. Montreal, Canada. **O30** Metastable equilibrium adsorption (MEA) theory: thermodynamic, sprectroscopic and quantum chemical development. G. Pan, <u>H. Chen</u>. Research Center for Eco-Environmental Sciences, Beijing, China. **O31** Ferroxane nanoparticles used for the fabrication of iron oxide ultrafiltration membranes: a new route for the synthesis of catalytic membranes? J. Rose, C. Levard, E. Tsui*, M.M. Cortalezzi*, J.Y. Bottero, A. Masion, Université Paul Cézanne, Aix Marseille, Aix en Provence, France, and *Rice University, Houston, USA. **O32** Solidification of liquid hydrocarbons in water by lithium carboxylate crystal fiber and the properties of the solidified aggregates. H. Sakaguchi, S. Hayashi, A. Kawai, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

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O33	Electro-osmosis remediation kinetics of heavy metal and radionuclide contaminated wastes and soils.
	B. Kornilovich, C. Abbruzzese [*] , N. Mishchuk, R. Klishchenko, A.V. Dumansky institute of Colloid and Water Chemistry, Ukrainian
	Academy of Sciences, Kiev, and *Institute of Environmental Geology
0.01	and Geoengmeering, Roma, Italy.
034	Executic field behavior in the course of an electroremediation of a soft
	S Amrate A Ait-Idir DE Akretche University of Science and
	Technology Houari Boumediene, Bab-Ezzouar, Algeria.
O35	A new concept in titanium dioxide photocatalyst for water
	purification.
	P. Araujo, G. Soler-Illia, M.A. Blesa, Comisión Nacional de Energía
	Atómica and CONICET, Buenos Aires, Argentina.
O36	Particle-bacteria interactions in a drinking water supply system.
	S. Tomlinson, E.A. Palombo, I.H. Harding, Swinburne University of
017	Technology, Australia.
037	Removal of lead (II) from kaolinite of Çanakkale (Turkey) by using
	A Altin M Decirmenci Zonguldak Karaelmas University Zonguldak
	Turkey.
O38	Methanogenic activity under different nickel forms.
	E.G. Fermoso, S. Mieves, P.N.L. Lens, Wageningen University, The
	Netherlands.
O39	Assessment methodologies for Copper and Zinc behaviour in a
	neutralsynthetic soil: pH influence.
	P. Hlavackova, <u>R. Barna</u> , M.A. Fernandez, Ecole des Mines d'Albi-
040	Carmaux, Albi Cedex 09, France.
040	J Fernández-Gálvez E Barahona MD Mingorance A Peña
	Estación Experimental del Zaidín, CSIC, Granada, Spain.
041	Kinetics of pollutants adsorption at solid/solution interfaces: a search
	for the theoretical background of the empirical pseudo first and second-
	order kinetic equations.
	W. Rudzinski, W. Plazinski, Marie Curie-Sklodowska University,
0.40	Lublin, Poland.
042	Kinetic analysis of Bioremediation of crude oil.
	I. Anrea, B.U. Oparaji, Rurai Airica Water Development Project, Imo
043	Surface characterisation of fungi and its implications to metal ion
010	adsorption.
	G.D. Bewsell, I.H. Harding, M. Molphy, W. Skinner, R.J. Crawford,
	Swinburne University of Technology, Hawthorn, Australia.
O44	Enhanced biotreatment of selenium via specialized bacterial groups.
	M. Lenz, I. Manconi, C. Roubos, A. Gmerek, P.N.L. Lens, Wageningen
o / F	University, The Netherlands.
O45	Chelate-assisted phytoextraction of Cu and Pb with the aid of organic
	MWH Evangelou M Ebol A Schoeffer DWTH Ascher Dislocio V
	Umweltbiologie und –chemodynamik. Aachen, Germany.
	· · · · · · · · · · · · · · · · · · ·

O46	Adsorption of freons by calcium carbonate under atmospheric
	Conditions. VS Zakharenko AN Messishuk* Instituto of Catalucis DAS
	Novosibirsk, and *Institute of Petroleum Chemistry, BAS, Tomsk.
	Russia.
O47	Colloidal mesostructures induced by interfacial non-homogeneities at
	the air-water interface.
	J.C. Fernández-Toledano, A. Moncho-Jordá, F. Martínez-López, R.
	Hidalgo-Álvarez, University of Granada, Spain.
O48	Influence of synthetic and biogenic surfactants on ligand-promoted
	dissolution of iron and aluminum oxides.
D 1	N. Carrasco, S.M. Kraemer, R. Kretzschmar, ETH Zürich, Switzerland.
PI	Role of organic matter on the mobility of radiocesium in agricultural
	SOII. V Nakamany N Ishikawa K Tagami S Hahida National Instituta
	of Radiological Sciences Inage-Ku Chiba-Shi Japan
P2	Water repellency kinetics and nature of wetting in urban soil samples
	G.E. Schaumann, D. Diehl, Technical University of Berlin, Germany.
P3	Influence of soil characteristics and evaporation processes on the
	raising up of salt and pollutants in mediterranean mining areas.
	J.M. Peñas, S.A. Gómez-Lopera, G. García, Technical University of
	Cartagena, Spain.
$\mathbf{P4}$	Characterization of soil and sediments from a Mediterranean mining
	area and its relationships with metal mobility.
	S.A. Gómez-Lopera, G. García, J. Cuadrado, Technical University of
Dr	Cartagena, Spain.
гə	M Ishiguro I Koopal [*] University of Okayama Japan and
	*Wageningen University The Netherlands
P6	Direct movie analysis of brownian motion of colloidal particle and its
	application to diffusion constants of small flocs.
	Y. Kusaka, Y. Adachi, Tsukuba University, Japan
P7	Deposition and subsequent release of Na-kaolinite particles by
	adjusting pH in the column packed with standard Toyoura sand.
_	K. Shiratori, Y. Adachi, Tsukuba University, Japan
P8	Restructuring of Small Flocs Formed with Polyelectrolytes.
DO	K. Aoki, Y. Adachi, Tsukuba University.
P9	sorption/desorption properties of neavy metals on montmornionite
	K Itami* I Vanaj** *Fukui Prefectural University **Kvoto
	Prefectural University Japan
P10	Enhancement of herbicide photodegradation in the presence of
	cyclodextrins and different soil colloidal components.
	E. Morillo, J. Villaverde, C. Maqueda, C., Instituto de Recursos
	Naturales y Agrobiología de Sevilla, CSIC, Spain.
P11	Ethylcellulose microspheres for reducing movement of alachlor in soil.
	F. Sopeña, A. Cabrera, C. Maqueda, E. Morillo, Instituto de Recursos
	Naturales y Agrobiología de Sevilla, CSIC, Spain.

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- P12 Effect of charged polyelectrolytes on the electrophoretic behavior, stability and viscoelastic properties of montmorillonite suspensions. M.M. Ramos-Tejada¹, C. Galindo-González², R. Perea¹, J.D.G. Durán², ¹University of Jaén, and ²University of Granada, Spain.
- **P13** Migration modelling of humic acids associated with Np(V) ions considering interaction kinetics and impact of colloids on safety assessment of high-level radioactive waste disposal.

S. Nagasaki, S. Tanaka, University of Tokyo, Japan.

P14 Experimental and theoretical study of montmorillonite-glyphosate surface complexes.

L. Tribe¹, R.M. Torres-Sánchez², M. dos Santos Alfonso³, ¹Penn State Berks, Lehigh Valley College, Tulpehocken, PA, USA, ²CETMIC CC49, M.B. Gonnet, Argentina, and ³Universidad de Buenos Aires, Argentina.

P15 The adsorption properties of Al-pillared bentonites.

M. Altunlu, S. Yapar, Ege University, Bornova-Ýzmir, Turkey.

- P16 Role of mineral dissolution of a natural sand in the tributyltin behaviour at very low concentrations.
 H.M. Rafidiarison, M. Bueno*, P. Behra, ENSIACET, Toulouse, and * Université de Pau et des Pays de l'Adour, Pau, France.
- P17 Retention of pesticides onto vineyard soils and a lignocellulosic substrate. Contribution to the improvement of the water quality.S. Boudesocque, E. Guillon, M. Applincourt, GRECI-UFR Sciences, France.
- **P18** Characterization of non-colored river water humic substances.

H. Kodama, S. Nagao, N. Fujitake, M. Fukushima, Masashi, N. Hukazawa, N. Hiromatsu, H. Kudoh, Y. Matsunami, Tohru, Kyoto Prefectural University, Japan.

P19 A Monte Carlo simulation study of the effects of ion size and valence, and polyelectrolyte concentration in mixed size and valence counterion systems of polyelectrolyte solutions.

S. Madurga¹, N. Merchán¹, C. Rey-Castro², J.L. Garcés³, E. Vilaseca¹, J. Puy³, F. Mas¹, ¹Barcelona University, ²Campus Universitat Autònoma Bellaterra, Lleida University, Spain.

- P20 Surface electrokinetic properties of clays in Okinawa.
 S. Ooi, K. Nakaishi, H. Tsuchida, J. Ohno, A. Horie, National Institute for Rural Engineering, Ibaraki, Japan.
- **P21** Influence of natural organic ligand to U(VI) reduction by Fe(II) in natural underground water environment.

M. Sato, T. Toraishi, S. Nagasaki, S. Tanaka, University of Tokyo, Japan.

P22 Water solubility enhancement of [60]fullerene in the presence of humic substances.

M. Terashima, S. Nagao, Research Institute for Humanity and Nature, Kyoto, and Hokkaido University, Japan.

P23 Coagulation and fractionation of dissolved iron in estuarine mixing zone: the role of aquatic humic substances.
 M. Terashima, T. Shiraiwa, S. Nagao, Research Institute for Humanity and Nature, Kyoto, and Hokkaido University, Japan.

P24	Surface thermodynamic studies on biomass adhesion during expanded bad adcomption of by products
	V. RamiReddy, R. Cabrera, V. Geneva, A. Fernandez-Lahore,
	International University Bremen GMBH, Germany.
P25	Uptake of heavy ions from residual water onto microgels.
	M.A. Barrero, L. Cantón, A. Costoyas, J. Ramos, A. Imaz, J. Forcada,
	University of the Basque Country, EHU, Donostia-San Sebastián,
	Snain
P96	Adsorption of MCPs on goethite and humic acid coated goethite
1 20	Autolo S Fiel D Conden A C Islogica D Lóng E Area
	J. Anteio, S. Fioi, D. Gondar, A.C. Iglesias, R. Lopez, F. Arce,
	Universidad de Santiago de Composteia, Spain.
P27	A model for the impact of root exudates on the fate of heavy metals in
	the rhizosphere.
	S. Klepsch, M. Puschenreiter, W.W. Wenzel, University of Natural
	Resources and Applied Life Sciences, Vienna, Austria.
P28	Kinetics of Cr (III) adsorption on activated carbons.
	O.L. Galushko, S.I. Lvubchik, E.S. Lvgina, A. I. Lvubchik, A.F.
	Dmitruk IM Fonseca VF Tretvakov SB Lyubchik IM
	Litvinenko Institute of Physical Organic and Coal Chemistry NAS of
	Ukraina Donatek Ukraina
D00	Electrolyingtic properties of concentrated suspensions with biological
1 29	entemporta
	ULL (C. C. C. C. C. C. C. C. C. L. L. C. L. C.
	J.J. Lopez-Garcia, C. Grosse ⁺ , J. Horno, University of Jaen, Spain, and
Daa	"University of Tucuman, Argentina.
P30	Heteroaggregation of oppositely charged polymer colloids studied using
	single cluster light scattering.
	J.M. López-López, A. Schmitt, A. Moncho-Jordá, R. Hidalgo-Alvarez,
	University of Granada, Spain.
P31	Effects of humic acid-oxide interaction on proton and metal ion
	binding to the complex of both colloids.
	T. Saito ¹ , S. Nagasaki ¹ , S. Tanaka ¹ , L.K. Koopal ² , ¹ University of
	Tokyo, Japan, and ² Wageningen University, The Netherlands.
P32	Amount of aromatic compounds adsorbed on different geomaterials.
	M. Houari, S. Ait Hamoudi, S. Chernai-Hamdi, B. Hamdi, Z.
	Kessaissia, USTHB, Alger, Algeria.
P33	Assessment of the reactive surface area of the soil oxide fraction.
	J. Antelo, T. Hiemstra, R. Rahnemaie, W.H. Van Riemsdiik.
	Wageningen University. The Netherlands.
P34	Interaction of pesticides with a surfactant-modified soil interface
	Effect of soil properties
	M C Hernández Seriano, I. Delgado Morono, M.D. Mingoranco, A.
	Doña Estación Experimental del Zaidín CSIC Cranada Spain
Dor	Ligand facilitated reduction of unanium by Eq. in acusous solution
F 90	England-factificated reduction of uranium by Fe in aqueous solution.
	1. Honda, T. Toraishi, S. Nagasaki, S. Tanaka, University of Tokyo,
Doa	Japan.
P36	Removal of herbicides from water by static and dynamic adsorption on
	carbon materials.
	M.V. López-Ramón, M.A. Fontecha-Cámara, C. Moreno-Castilla,
	University of Granada, Spain.

P37	Adsorption of surfactants at the air-solution interface: theoretical description of adsorption equilibrium and kinetics.
	A. Andrzejewska, M. Drach, J. Narkiewicz-Michalek, Marie Curie- Sklodowska University, Lublin, Poland.
P38	Co-adsorption of cationic surfactants and antioxidants on the
	hydrophilic silica surface.
	A. Andrzejewska, J. Narkiewicz-Michalek, M. Szymula, Marie Curie- Skłodowska University, Lublin, Poland
P39	Colloidal characterisation of leachate from contaminated retention
	pond sediments column.
	B. Durin ¹ , P. Le Coustumer ² , B. Stolpe ³ , B. Béchet ¹ , M. Legret ¹ , P. Le Cloirec ⁴ , ¹ Laboratoire Central des Ponts et Chaussées, Bouguenais, France, ² Centre de Dévelopment des Géosciences Appliquées, Talence, France, ³ University of Göteborg, Sweden, ⁴ Ecole des Mines de Nantes,
	France.
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	Ukrainian State Agroecology University, Zhytomyr, Ukraine

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ABSTRACTS (Plenary and oral)

PL1

Ion binding to humics and minerals

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The principles of ion binding to humic substances (HS) and mineral oxides (MeOx) and the various aspects of modeling used in general-purpose speciation programs will be discussed. The discussion will focus on chemical and electrostatic interactions and the complications inherent to ion binding in multi-component systems. First binary systems (HS/ions and MeOx/ions) will be discussed and then ternary (MeOx/HS/ions).

An accepted model for the binding of cations to humics is the Non Ideal Competitive Adsorption (NICA)-Donnan model. The "chemical" parameters of the model are the site density, the median affinity constants for the ions, the ion binding stoichiometry, the width of the affinity distribution, the "electrostatic" parameter is the Donnan volume. Results obtained for purified humic acid are presented together with model predictions. The model has the ability to adjust to different heterogeneities and stoichiometries and accurately predicts ion competition.

The CD-MUSIC-Stern-Gouy-Chapmann (SGC) model is well suited to describe both anion and cation binding to mineral oxides; it incorporates information from crystallography, spectroscopy and surface chemistry. The "chemical" parameters are the site densities and the binding constants, the "electrostatic" the charge distribution of the ions and SGC characteristics. Some results for ion binding to Goethite will be presented. Key features of the model are its ability to adjust to the charge distributions of ions (binding type and stoichiometry) and the detailed prediction of ion competition.

In ternary systems HS and MeOx strongly interact and due to this cation and anion binding is not equal to the sum of the binding in the corresponding binary systems. An important consequence of the HS-MeOx interaction is that, in principle, the primary proton charge of both HS and MeOx particles adapts due to the fact that the electric field of the particles has changed. The effect will become stronger when next to the electrostatic interactions also complexation occurs between the HS functional groups and the MeOx surface sites. Models based on polyelectrolyte adsorption theory indicate that the adaptation is substantial. Changes in the degree of protonation of HS and MeOx will affect the binding of the other ions and vice verse and the extent of adaptation is directly related to the affinity between the HS and MeOx. This indicates that we have to deal with a rather complex problem. Modeling attempts that specifically address the MeOx/HS/ion system are only very recent.

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Polyelectrolyte adsorption at colloid surfaces. Monte Carlo simulations for the rational formulation of water-based flocculants

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Due to their fascinating, complex and important modifications of colloidal solutions and interfaces, transport processes, polyelectrolyte chains (such as synthetic polymers, polysaccharides, proteins) and oppositely charged colloids (such as organic and inorganic particles found in natural systems) stimulate a great interest in soft condensed matter, biology, environmental chemistry and industrial applications. In particular applications in the field of purification of water as flocculating water insoluble mixtures, adhesion, and powder processing are numerous and extension to gene therapy and bioengineering is today under consideration. In particular in natural environments, interactions between inorganic colloids and polysaccharides and the resulting complexation processes are expected to control the coagulation of colloidal material in suspension and the fate and transport of trace pollutants associated to them.

However, the long range attractive and/or repulsive character of electrostatic interactions between polyelectrolytes and colloids, solution and interface chemistry, chemical composition of the different species, geometry and concentration of both polyelectrolytes and colloids, etc, give these solutions specific properties which are partially understood. Thus, so far, little is known in the rational use of polyelectrolytes with oppositely charged colloids when for example polyelectrolytes are used as polymeric flocculants.

Owing to the important potential of computer simulations to provide qualitative and quantitative means of understanding the factors that could influence polyelectrolyte chains and colloid interactions, we describe here a Monte Carlo approach to get insight into the behaviour of a flexible, semi-flexible and rigid polyelectrolyte with the presence of an oppositely charged colloid. The adsorption/desorption limit which is a key parameter for colloid surface description and applications in water treatment of polyelectrolyte/particle mixtures is also investigated. The polyelectrolyte conformations are analysed prior to and after adsorption, the polymer interfacial structure is investigated as well as the particle surface coverage and polyelectrolyte adsorbed amount. Given the need to identify, understand and monitor parameters which are related to flocculant s performance, new polyelectrolyte architectures are also presented.

"Complex Formation between a Nanoparticle and a weak Polyelectrolyte. Monte Carlo Simulations" S. Ulrich, A. Laguecir, S. Stoll, Journal of Nanoparticle Research, 6, 595-603, (2004).

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O2

Neither "adsorption" nor "partitioning": a link disruption model for organic compound-soil organic matter interactions.

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Although the importance of interactions between organic compounds and soil organic matter (SOM) can hardly be overestimated, sorption mechanisms are far from understood due to the complexity of the chemically and physically heterogeneous SOM sorbent phase. Structure of the SOM sorbent can be changed drastically as its hydration status varies under different environmental conditions. To understand the SOM hydration effect on sorption, insights into SOM-organic compound sorption mechanisms are required, and, vice versa, comprehending the effect of hydration (or solvation, in a wider sense) on organic compound sorption by SOM is helpful in delineating sorption mechanisms in such a complicated and important environmental sorbent. On the basis of a series of sorption studies, we present a concept elucidating the relationship between the hydration effect on organic compound sorption by SOM, and sorption mechanisms. The central point of this concept is based on the observation that for certain compounds, sorption strongly increases upon SOM hydration (or solvation by strongly interacting organic solvents). This phenomenon is interpreted by considering the SOM phase to be represented by a set of distributions of various inter- and intra-molecular non-covalent links and contacts. Hydration (solvation) of SOM is associated with partial disruption of the linkages and SOM swelling, resulting in some SOM structure opening. The "quasi-equilibrium" of this link disruption and the extent of the opening of the SOM structure shift as a function of organic compound sorption, and are assisted by solvation of disrupted link fragments, thus involving cooperation between solute and solvent molecules. Depending on the ability of sorbate molecules to interact with SOM and to compete with water molecules for sorption sites, there will be a trade-off between solvent-assisted penetration of organic compound molecules into SOM linkages, versus competition between sorbate and solvent molecules for new sites at those disrupted contacts.

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O3 Smectite suspension structural behaviour

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Smectite suspensions are known to be naturally high in volume, providing interesting stability properties to the suspension. In order to further our understanding of the structural properties of smectite suspensions, microscopic analysis, particle sizing and electrochemical studies were conducted in the absence and presence of calcium ions.

The equilibrated state of a smectite suspension in the presence of Ca(II) greatly influences smectite stability. Adequate time is required to allow suppression of the initial swelling of the smectite, full cation exchange and platelet aggregation. At low Ca(II) concentrations, smectite particles are colloidally stable due to electrical double layer repulsion caused by the net negative charge of the platelets. At high Ca(II) concentration, above the cation exchange capacity, the smectite stability decreases as time-dependent ion exchange of calcium alters smectite from the sodium to the calcium form. Both ion exchange and restriction of the double-layer repulsion retards the swelling process. Upon introduction of calcium ions, the platelets form 2 um randomly orientated, coagulated aggregates with a high presence of edge-face orientation. As ion exchange continues to occur, the platelets increase in orientation forming a honeycomb structure with edge-edge and edge-face orientation.

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O4 Do biofilms affect the water repellency of urban soil samples?

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Water repellency is an important phenomenon in soil systems and is influenced by physical, chemical and biological factors. Studies on the influence of bacteria or surface- attached bacteria (biofilms) on soil water repellency are rare. Especially, the role of bacterial EPS in soil water repellency has not been investigated until now.

In this study, we investigated the influence of hydrophilic and hydrophobic bacteria on soil wettability. Three different soil bacteria, Variovorax paradoxus, Bacillus sphaericus and an α- Proteobacterium, were investigated in different states (vegetative cells and spores in the case of Bacillus sphaericus). The bacteria, isolated from urban soils in the Berlin Tiergarten Park and from a sewage field (in Berlin-Buch), were grown in a bioreactor on sterilized soil samples and in batch cultures on four different synthetic materials with hydrophobic and hydrophilic surfaces, to form biofilms. Surface hydrophobicity of the overgrown material was determined by the water contact angle, and cell surface characteristics of bacteria were measured using the zeta potential and a hexadecane-two-phase-system.

The α-Proteobacterium and Variovorax paradoxus were classified as hydrophobic, and Bacillus sphaericus was classified as hydrophilic. Contact angles of the overgrown artificial material showed a significant influence of the respective material, but differences between the bacteria were not significant. The differences between the materials may be due to effects of the material on biofilm growth or EPS properties. The bacterial EPS of the hydrophobic α-Proteobacterium were more hydrophilic than the cell walls, while those of Bacillus sphaericus were less hydrophilic. In contrast to the artificial materials, differences in contact angle for the inoculated soil sample showed differences between bacterial strains. significant $_{\mathrm{the}}$ The α:-Proteobacterium was able to hydrophobize the soil sample, while Bacillus sphaericus showed significant hydrophilisation. The results clearly demonstrate the effect of bacterial biofilms on soil wettability.

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PL2

Interactions of metals with heterogeneous matter

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Different methodologies aimed at describing metal interactions with heterogeneous matter have been developed. A simple and general way of describing multiple complexation equilibria consists in determining the stoichiometric equilibrium constants. For macromolecules with a large number of sites, protonation constants can be easily determined by simply replotting the binding curve[1]. An extension of this procedure to multicomponent systems allows the determination of the combined metal and proton stability constants. Binding data of Ca to PAA will be used to exemplify this procedure.

Interactions with heterogeneous matter can also be described by means of adsorption isotherms^[2]. A physical insight into this procedure can be obtained by looking at the underlying affinity spectrum, the distribution of affinities that characterise the binding properties of the ligand. For monocomponent adsorption, this distribution has been obtained by numerical regularization, semi-analytical and analytical procedures. Results obtained indicate that in a wide range of intermediate coverages, the coverage is mainly dependent on the first moments of this distribution [3]. The computation of these moments provides, thus, a meaningful way of understanding the binding characteristics. Extension to cases of multicomponent (i.e. competitive) adsorption has been reported [4-5]. Thus, the mean affinity, variance and covariance of competitive isotherms like Frumkin or NICA have been obtained. Affinity spectra and characteristic moments of the NICA or Frumkin description of the binding of Cu, Zn, Cd to Humic acid will be presented. Potentiometric and voltammetric titrations have been used in these studies and specific procedures to recover the binding curve from voltammetric data have been developed [6]. Complementary, a new voltammetric stripping technique called AGNES has been developed to measure the free metal concentration [7]. A last point will be devoted to develop the concept of the conditional affinity spectra, the apparent distribution of affinities seen by a metal ion at some fixed pH [8]. Conditional affinity spectra for Frumkin or NICA isotherms will be presented. The dependence of the properties of these affinity spectra with pH will be analyzed, emphasizing that some properties of the multidimensional spectra can be obtained from the behaviour of the conditional isotherms.

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O5

Nature and interactions of black carbon surface with organic contaminants and implications for environmental risks

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Charred or partially charred materials and soot particles produced during combustion processes and generally referred to as Black carbon. Black carbon is increasingly being recognized as an important component of soil organic matter in many soils and sediments from the regions that experience frequent-fires or receive input form partial combustion processes. For example, in some Australian, German and Brazilian soils, up to 40% of the total organic carbon has been found to consist of charcoal. Being relatively resistant to degradation (often termed as non-labile or inert pool) it can persist in the environment on geological time scales. The terrestrial char often finds its way to marine or freshwater aquatic ecosystems, facilitated by wind and water movement. Our research has shown that the black carbon has very strong affinity for contaminants, depending on their nature and properties. Depending on the origin, the black carbon can serve as an efficient sinks for organic contaminants, such as pesticides, polynuclear aromatic hydrocarbons, in both terrestrial and aquatic ecosystems. We have also observed that both sorption and desorption of organic contaminants is strongly linked to the nature of black carbon. Using solid-state 13C nuclear magnetic resonance (NMR) with cross-polarisation (CP) Magic-Angle Spinning (MAS) and bloch decay (BD) as well as other spectroscopic techniques, we have been able to characterize the nature and properties of black carbon and relate these to the nature of interactions with organic contaminants. In this presentation, behaviour of organic contaminants will be discussed in relation to the nature and properties of the black carbon.

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O6 Picloram adsorption on clays

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Pesticides are widely used for control of broad-leaf weeds and other vegetation. The behavior of pesticides in soil is a largely dynamic phenomenon. After application, they may pass into streams, rivers and lakes or leach through soil with the possibility of contaminating subsurface waters. In a first approximation, soils can be considered as a combination of the minerals that compose them. Thus, pesticides also may be adsorbed onto soils components such as clays. In particular, montmorillonites have shown a great capacity of adsorption of both metallic cations and organic substances due to their small particle size (<2 m), high surface area and isomorphic substitutions in their structure. The study of the interaction parameters associated with adsorption and desorption will provide a thermodynamic database that will be useful to predict the environmental fate and behavior of pesticides.

Four types of clays were choose due to the different structural characteristics, montmorillonites (Wyo and 428), nontronite, illite and kaolinite and they were physical-chemical characterized by several methods. The purity determined by the Rietveld method is higher than 98% for all the samples confirming the superficial analyses carried out by EDAX. The morphology of the particles observed by electronic microscopy corresponded to the suitable ones in the bibliography of the topic. The specific interlayer surface of the clays was calculated as the difference between the total surface measured by water adsorption (SW) and the external surface determined by N2 adsorption (BET method, SN2). The specific interlayer surface determined for Wyo, 428, nontronite, illite and kaolinite were 611, 496, 548, 25 and 15 g/m2 respectively. The IEP values obtained for Wyo, 428, nontronite, illite and kaolinite were, 3.2, 1.0, 5.1, 7.1 and 2.5 respectively.

XRD of the dry and wet samples (P/P0=0.47) were also carried out. The influence of the water content in the interlayer, was measured by a d(001) reflection parameter shift, indicating the interlamellar space size for the expandable samples like montmorillonites and kaolinite. Due to the influence of the pH on the montmorillonites structures XRD were also carried out at different pH values, not being evidenced of notorious crystalline modifications. The values of CEC were 306; 305; 294; 214 and 39 meq/100g for Wyo, 428, nontronite, illite and kaolinite, respectively.

Picloram, 4-amino-3,5,6-trichloropicolinic acid is a herbicide from the picolinic acid family and is used for broadleaf weeds control in wheat, barley crops and woody plants on rights-of-ways. Picloram adsorption isotherms were measured

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by UV-Vis spectrophotometry at 223 nm. Surface coverage was calculated by the difference between initial concentration and the concentration remained after 24 hs equilibrium. The adsorption dependence with pH was also measured and the thermodynamic adsorption parameters were calculated.

Interactions of organic compounds in hydrated and "non-hydrated" organo-clay phases: sorbate-water competition

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Modified clays (organoclays) prepared by the exchange of organic cations with a native exchangeable cation, enjoy wide attention due to their potential use in adsorption and catalytic processes, engineering schemes for waste water treatment, prevention of environmental pollution and in other applications. The hydrophilic/hydrophobic balance of organoclay "surfaces", potential forspecific interactions and complex formation with various organic molecules can be regulated by varying the clay type and the structure of the exchangeable organic cation. Solvents and, specifically, water are obvious co-participants in the sorption process at organoclay surfaces. The presence of water may involve competition with organic sorbates, cause a change in sorbent polarity and cation solvation, result in water bridge formation, and create greater available surfaces (or volumes) due to breaking up of the organoclay aggregates or hydrationinduced swelling. Hence, there is a need for quantifying the overall water effect on sorption of organic compounds on organoclays. Surprisingly, there are very limited data on the comparison between the thermodynamics of sorption of organic compounds on non-hydrated (essentially non-solvated) and on completely hydrated organic cation-exchanged clays. The present work examines the effect of hydration on interactions of selected model organic compounds with model organoclays. The approach chosen for establishing the hydration effect is based on comparing equilibrium sorption isotherms of a compound on a completely hydrated sorbent (suspension in water) and on a non-hydrated (dehydrated) sorbent immersed in a non-polar inert solvent - n-hexadecane. This comparison provides a measure of the overall effect of the solvent (water) on the thermodynamics of the transfer of the sorbate from a bulk solvent phase to a (solvated) sorbent. In order to evaluate the solvent effect on sorbate interactions in a sorbent phase, differences between solute-water and solute- nhexadecane interactions had been eliminated by comparing aqueous and nhexadecane-based sorption isotherms, using a solute activity scale. HDTMA (nhexadecyl-trimethylammonium)-exchanged bentonite was chosen as the model organoclay. The probe compounds were selected to form a series of sorbates with increasing ability to undergo molecular interactions as indicated by the sorption measurements on the non-hydrated sorbents from an inert solvent. Using this procedure, it was found that organoclay hydration significantly suppresses the interactions of the less "polar" organic compounds, in agreement with earlier observations for water-competitive sorption of non polar organic compounds by short organic chain-based organoclays. In contrast, sorbent hydration may have no distinct reducing effect on interactions (or may even enhance interactions) of organic sorbates capable of stronger specific

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interactions. The disappearance (or diminishing) of a hydration-induced suppressive effect on interactions correlates with an increasing potential of a sorbate to undergo molecular interactions and to compete effectively with water for sorption sites. The competitive effect of water is more pronounced at lower sorbate uptakes/activities and can disappear at higher sorbate activities. It appears that a "simple" mechanistic vision of the interactions of organic compounds in the organoclay phase based on sorbate-solvent competition is sufficient to understand the hydration effect without recourse to other ways the presence of water may influence the system.

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Study of the stability of concentrated aqueous clay/magnetite suspensions

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The most abundant inorganic colloid particles in water systems are clays and metal oxides. The former colloids play a very important role in the structural stability of soils, the behaviour of sediments in natural waters, and the mobility of colloids in soils and aquifers. In addition, the colloidal clay that remains dispersed in water can enhance the transport of adsorbed contaminants.

In this work, we carry out an analysis of the stability of concentrated aqueous suspensions composed of micron-sized clay particles and magnetite nanoparticles. The clay mineral employed was sodium montmorillonite and the magnetite nanoparticles were synthesised by the coprecipitation method described in [1]. The pH and ionic strength of the aqueous suspensions were, respectively, 3 and 2×10^{-3} mol/L NaNO₃. Under these conditions, magnetite nanoparticles are adhered to the clay particle surface.

The study of the stability of dilute suspensions of clay/magnetite particles was performed in a previous work [2], using optical techniques. Nevertheless, this method is not suitable in the case of concentrated suspensions, because of their opacity. In order to analyze the stability of these suspensions, we have performed a new experimental method [3] based on electromagnetic induction phenomena. The resonant frequency in a parallel LC circuit, in which a sensing coil surrounds the test tube that contains the clay-magnetite suspension, was measured as a function of time and height in the measuring test tube. Using this method, the stability of the clay/magnetite suspensions was studied varying the total volume fraction of solid particles, and the (magnetite volume fraction / clay volume fraction) ratio.

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O9 SANS studies of natural aquatic colloids

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Aquatic colloids - naturally-occurring, often heterogeneous, aqueous colloidal systems which may contain both organic and inorganic components - are of considerable environmental interest because of their interaction with pollutants and the role that they play in the biogeochemical cycling and bioavailability of these pollutants. Furthermore, the introduction of new legislation, such as the Water Framework Directive in Europe [1], brings new challenges for environmental protection and regulation, and places new demands on our understanding of these natural colloidal systems.

In recent years it has become increasingly clear that the established methods of colloidal characterisation employed in the environmental sciences - mostly based on imaging, microscopy, static and dynamic light scattering, and physical separation methods - do not provide the whole picture. A sizeable proportion of the aquatic mass transport appears to involve material with length scales <0.2 um. Such nanoparticulates do, however, readily lend themselves to study by small-angle X-ray (SAXS) and neutron (SANS) scattering.

The challenge is that in terms of concentration, and size and compositional polydispersity, natural aquatic colloids are far removed from the "comfort zone" afforded by most model colloidal systems (eg, polymer laticies, or silica dispersions). Perhaps because of this there have been relatively few SAXS/SANS studies of these systems to date, and most of those have only concentrated on the humic substances [2,3]. Nonetheless SANS offers the potential, perhaps through the use of contrast variational methods, to investigate how the humic and mineral components combine to determine the overall flocc structure in the aquatic environment. Work is now in progress to address this key issue.

This presentation will show how SANS has been used to investigate a range of environmental samples and source materials, including river waters and bed sediments, soils, field drainage runoff and agricultural slurry. Preliminary analysis of the data has already shown, as expected, that interpretations based on the nanoparticulates having discrete regular morphologies are inadequate. One potentially significant observation has been that none of the systems so far studied demonstrate structures that are consistent with diffusion-limited or reaction-limited aggregation processes.

Future work will also investigate the effect of varying the matrix chemistry, temperature and flow conditions.

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Particle network formation in soils: is there aggregating or dispersing effect of humic substances?

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The structure of soils develops in the gradual aggregation of mineral particles under variable conditions. The organic matter content and the ionic composition of soil solutions have dominant effect on soil structure. The structure of particle network in soils, the retardation or release of colloidal particles, their mobility and transport are inherently influenced by natural organic matter bound to the mineral matrix. The presence of cementing cation like calcium is essential for the formation of bridges between mineral particles and also between organic matter and mineral phase. Therefore, not only the mineral constituents and the organic matter content, but also the composition of soil solution is responsible for the physical structure formed in soils.

Humic acids can be bound to the most reactive surface sites of clay and oxide particles, i.e. to Al-OH mainly at the edges of clay lamellae and to Fe-OH on iron oxides, in surface complexation reaction. The permanently and/or conditionally charged clay minerals (mainly montmorillonite) and iron oxides (hematite and magnetite), as known major mineral components in natural systems, were selected to study the particle interactions in composite systems containing humic acid in the absence and the presence of calcium ions. Several soil samples from long term and remediation experiments were also investigated in parallel, and compared in respect of their organic matter and calcium contents. Adsorption (the accumulation of organic and inorganic ions at mineral/water interface) was quantified, the charge state and aggregation of particles were measured by means of electrophoresis and dynamic light scattering, and rheology was used to characterize the particle network formation.

In the mixed systems, strong heterocoagulated network of oppositely charged clay and oxide particles forms in acidic pHs, since the small oxide particles act as adhesive between clay lamellae. This structure can be broken down if relative small amount of humic acid is added to the systems, or cannot build up in presence of humic acids. Humic substances have dispersing effect in clay and mixed iron oxide-clay suspensions due to the complexation and recharging of surface hydroxyls of solid particles in the absence of bi- and multivalent cations. The humus coating on both natural soil and specimen mineral particles results in steric and electrostatic stabilization of particles. However, the mineral particles become aggregated in the presence of calcium ions, especially, if both humic acid and calcium ions are in optimal ratio in the clay and mixed iron oxide-clay suspensions, in which a strong particle network with high shear tolerance can build. The aggregation of mineral particles is enhanced by the joint effect of humic acid and calcium ions, since organo-mineral complexes form

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through calcium-bridges. The higher organic matter content the higher amount of calcium addition is expected to reach the optimal aggregation.

A systematic study on the relevant model systems helped us to clarify the ionic, molecular and particle interactions, which are responsible for particle network formation in soils, where sand fraction being present even more than 50% does not play any role.

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Evaluation of amphiphilic properties of fulvic acid and humic acid by alkylpyridinium binding study

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Amphiphilic properties of humic substances are evaluated through the study on the binding of N-alkylpyridinium bromide (CnPy+Br-, n = 12, 14, 16), using a potentiometric titration method with surfactant-ion-selective membrane electrodes in aqueous solution. Different binding behaviors are observed between FA and HA due to the differences in the density of carboxylate groups as well as hydrophobicity-hydrophilicity balance. Independent sites binding behavior is observed in the CnPy+-HA system, however, cooperative binding is observed in CnPy+-FA system. The binding of CnPy+ to HA is stronger than that to FA, reflecting the importance of hydrophobic interaction between surfactant molecules and the backbone of HA molecules. The effects of chain length of surfacants, pH, ionic strength, and temperature were also studied to reveal the amphiphilicity of humic substances.

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A new method to characterize interactions between counter ions and charged particles via Wien effect measurements in dilute suspensions

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The electrical conductivity (σ) of an electrolytic solution is expected to be independent of the applied electrical field strength (E) according to Ohm's law, and the deviation from this when σ increases with increasing E is known as the Wien effect. With the help of a custom made, low-cost apparatus yielding a short (about 10^{-5} s) high-voltage pulse that enables electrical fields of up to 2 x 10^7 V/m [1], we have measured the increase in $\sigma(E)$ of mono and divalent cationic electrolyte solutions and suspensions made of pure clay minerals and clay fraction (< 2 μ m) particles separated from natural soils. The electrical conductivity increase of the clay suspensions with increasing E was up to fourfold [2,3]. This general trend for increase can be explained by a greater dissociation of the counter ions from the particles, thus increasing the contribution of those ions to the overall σ of the suspension. In this sense the variation of σ with E reflects the "bonding strength" of the counter ions to the charged particles. Other possible mechanisms contributing to the measured, increasing $\sigma(E)$ functions are the joule heating, the rotation of the platy clay particles and their alignment with the applied electrical field, and the slipping plane encroaching on the particle surface. In this lecture we will discuss these possible Wien effect mechanisms and try evaluating their separate contributions to the overall measured $\sigma(E)$ increase for different exchangeable cations, ionic strengths and particle concentrations. Next, we will describe $\sigma(E)$ measurements with homoionic montmorillonites saturated with mono- and divalent cations and discuss the correspondence between the Wien effect results and known properties of diffuse double layers. We will also propose a new, simplified thermodynamic interpretation of the Wien effect measurements in terms of mean free Gibbs bonding and adsorption energies, and demonstrate it for evaluating the adsorption energies of mono- and divalent cations on vellowbrown and black soil particles [4]. Finally, we will report in brief on: 1. Applying Wien effect measurements for characterizing the adsorption interactions of both cations ("counter ions") and anions ("co ions") with variable charge soil particles [5]; 2. The observed phenomenon of negative Wien effect – a decrease of the $\sigma(E)$ relationship towards a local minimum at intermediate field strengths and its subsequent increase at higher E; and 3) An application for heavy metal cations (Pb, Cu, Cd) adsorption on soil particles.

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Velocity of rising bubbles as a method of detection of organic contaminations in water

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Adsorption at water/gas interface is a typical feature of surface active substances and organic contaminants of water. Velocity of bubbles rising in liquids depends mainly on viscosity of the liquid, density difference, bubble size and state of the liquid/gas interface. Presence, often even traces of surface active substances, can lower the bubble rising velocity up to 50%, due to retardation of the liquid/gas interface mobility. In clean water, where the interface is fully mobile, the bubble velocity is higher than velocity of solid sphere of identical diameter. In solutions of surface active substances (SAS) the adsorption layer is formed at the bubble surface and as a result of the bubble motion a non-uniform distribution of the adsorbed molecules and surface tension gradients are induced there. These surface tension gradients retard mobility of the bubble gas/liquid interface and as a result the hydrodynamic drag is increased and the bubble velocity is lowered.

The paper presents results of studies on influence of model surfactant (npentanol) and commercial detergents ("Ludwik" nad "Vizir") on velocity of the rising bubble. A simple and non-expensive method for detection of surface active contaminations presence in water, elaborated on the basis of these measurements, is presented as well. The commercial detergents were used as "models" of surface active contaminations in water reservoirs. To determine profiles of the local velocity of the rising bubbles and values of the terminal velocity a motion of single bubbles detaching from the capillary was recorded as a function of distance, using the CCD camera coupled to MotiCam 2000 digital recording system and the stroboscopic illumination. The movies recorded were analysed frame-by-frame using the image analysis software. It was showed that the terminal velocity of the bubbles decreased rapidly with increasing concentration of the solutes studied from 34.610.2 cm/s in distilled water to c.a. 16 cm/s. In the case of the commercial detergent "Ludwik" the bubble terminal velocity was only 16.4 cm/s at its concentration of 10-2 g/l only. Thus, measurements of the time of passage of a long enough distance by the rising bubble can be used as a method of detection of the organic contaminations in water. The set-up consisting of long glass column (150 cm) with the capillary at bottom, compressed air container and valves (to control gas supply) was built and the time of passage of distance 140 cm by the rising bubble was measured using the stop-watch. It was found that values of the bubble terminal velocity determined in this simple set-up were in a good agreement with the CCD MoticCam results. Thus, the set-up and the procedure elaborated can be used as a simple, quick and non-expensive method for detection of water surface active contaminations. Sensitivity of the method elaborated was also tested on samples of water from a few polish water reservoirs and a presence of organic

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contaminants was detected there (the bubble terminal velocity was lowered by 10-50%).

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Rheological properties of dilute suspensions of montmorillonite

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Rheological properties of aqueous suspension of mointmorillonite are very unique and have received many interests. However, most studies reported so far are carried out for concentrated suspensions where mechanical analyses on the basis of colloidal interactions are expected to be complicate. In the present study, our attention is focused on the dilute suspension of momorillonite in order to carry out simplified analysis in viscosity and yield stress in terms of microstructure and colloidal interactions. In the analysis, three important regimes; electrostatistically stable, intermediate and coagulate, are found to be treated separately.

In the first regime, due to high surface charge density, the effect of diffusive double layer interaction is significant either for viscosity and yield stress. Using two-plate model of double layer repulsive force, the yield stress can be expressed as a function of volume fraction monmorillonite and ionic strength. The measured data using rotary vane viscometer verified the validity of our model.

In the second regime, so-called edge-face and face-face interaction can explain our data of viscosity and yield stress against pH. However, quantitative interpretation is still obscure. That is, so-called edge-face interaction can not be explained without artificial parameter.

In the analysis of the last regime, the spiral-type capillary viscometer was constructed to detect the small difference due to the weak strength of flocs formed in different chemical environment. Analyses were carried out referring the data of floc structure obtained by sedimentation velocity against floc diameter. So-called tactoid array structure was detected when the species of counter ion is Ca.

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PL3 Electrokinetics of particles with complex surfaces

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Recently the author has presented a general electroacoustic theory for the macroscopic electric field in a dilute suspension of spherical colloidal particles in an electrolyte solution (Ohshima, Langmuir, 2005, 21, 2000). It is shown that the macroscopic field in the suspension consists of the colloid vibration potential (CVP) and the ion vibration potential (IVP), induced by an oscillating pressure gradient field due to an applied sound wave. This is a unified theory that unites previous theories for CVP and those for IVP. Approximate analytic expressions are derived for CVP and IVP. The obtained IVP expression agrees with Debye s formula that is corrected by taking into account the force acting on the electrolyte ions as a result of the pressure gradient in the sound wave. In the present paper, following the idea of Duval et al. (Environ. Sci. Technol. 2005, 39, 6435) that humic substances are soft particles, that is, hard particles coated with an ion-penetrable surface layer of polyelectrolytes (Fig. 1), we develop a theory of electroacoustics in a dilute suspension of spherical soft particles as a model for humic substances. We derive approximate analytic expressions for CVP and IVP in a suspension of spherical soft particles. The obtained analytic expression for the CVP of soft particles involves the softness parameter as well as the density of the fixed charges distributed in the polyelectrolyte layer on the particle surface. This theory covers the CVP of hard particles and that of spherical polyelectrolytes, since a spherical soft particle becomes a spherical hard particle in the limit of no polyelectrolyte layer while it tends to a spherical polyelectrolyte in the absence of the particle core.



Fig. 1. Soft particle as a model for humic substances

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Factors influencing the rates of formation and dissolution of amorphous iron oxides in aquatic environments

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Amorphous iron oxides (AFOs) are ubiquitous in natural aquatic environments and play a key role in both the bioavailability of iron - a key micronutrient for all living organisms - and in the transport and fate of contaminants adsorbed to their surface. Factors influencing the rates of formation and dissolution of AFOs are thus critical to the intrinsic functioning of ecosystems and to man\s impact on these systems. Iron species in aquatic systems may undergo a variety of transformations (oxidation-reduction, complexation-dissociation, hydrolysis, precipitation and dissolution, adsorption-desorption) many of which influence the formation and reactivity of AFOs. In this presentation, attention will be given to examination of recent advances in understanding key processes influencing amorphous iron oxide formation and dissolution kinetics. Particular attention will be given to the effect of organic complexation and pH on rate of AFO formation and photochemical and biotic mediation of AFO dissolution with insights drawn, in part, from the work of Rose and Waite (2003, 2005), Waite (2005), Fujii et al. (2006), Salmon et al. (2006) and Pham et al. (2006).

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Breakthrough of mercury in a presence of a natural quartz sand: Influence of pH, buffer, organic matter and initial mercury concentration

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Mercury (Hg) is one of the most toxic metals in the aquatic environment. Even at very low concentration, its high toxicity makes it an environmental threat in industrial, mining, and domestic wastes. Hg can be complexed by organic matter in sediments, making Hg behaviour very complex to predict. Fineparticle materials that present a large surface area such as oxides, oxyhydroxides and silicates are among the principal sorbents of the metal species. Thus, sorption, diffusion and precipitation reactions at the mineral-waer interface can significantly retard the release of metal ions into the aquatic systems. Degradation of groundwater quality by Hg migration from polluted soils and sediments has to be considered. Knowledge of sorption interactions at the solid-liquid interfaces is a prerequisite for understanding the mechanisms of contaminant fate and transport in the subsurface compartment.

For this purpose, the sorption of Hg was investigated during its migration through a column filled with a quartz sand from an alluvial aquifer. This sand was heterogeneous and contained clays and hydroxides at its surface. The reactivity of a mineral sorbent toward a contaminant can thus be very different whether it is pure or not and varies with specific surface area and chemical composition of colloid coatings. Sorption of trace elements on such heterogeneous sorbents can be positively correlated with one of their mineral coatings. Besides modification of the surface reactivity, laboratory experiments have shown that natural colloids can be easily mobilized by chemical perturbations of the pore water. Thus, contaminants associated with colloids can be transported through subsurface environments. The main objective of this study was follow the sorption of Hg onto quartz sand (pure and natural) as a function of pH and initial Hg(II) concentration.

Hg sorption onto a sand of natural origin could be explained assuming the presence of three sorptive surface sites, i.e., silica, hydroxides and clays. Hg affinity for hydroxides being much greater than for clays and silica. Furthermore, we showed that the Hg concentration on the colloidal fraction (clays or organic matter) as compared to the remaining sand fraction was high. This result has an important environmental significance because this type of colloidal material can be easily mobilized due to physicochemical perturbations.

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These mobile colloids can thus enhance the transport of Hg sorbed on their surface

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O17 Formation and breakage of hydrous ferric oxide aggregates

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Precipitation of hydrous ferric oxide (ferrihydrite) is important in the aquatic environment for a number of reasons, for instance in the adsorption of various dissolved impurities. Ferric salts are also widely used as coagulants in the treatment of water and wastewater, where their action may greatly depend on the formation of an amorphous precipitate. In the present work the aggregation of precipitate particles from dilute Fe(III) solutions has been studied by a dynamic monitoring technique which gives continuous information on aggregate size.

Experiments were conducted under controlled shear conditions in a stirred vessel, with continuous monitoring. Aggregates (flocs) were formed under quite low shear conditions (mean shear rate up to about 50 s-1). Under these conditions flocs grow to a limiting size, depending on their strength and the applied shear. When the limiting size had been reached the shear rate was increased to a much higher value (typically around 500 s-1). In many cases the step increase in shear rate caused an immediate and rapid decrease in aggregate size, as a result of breakage. This provides a convenient empirical method of quantifying floc strength. Following a short period of high shear, the stirring rate was reduced, in order to allow re-growth of flocs. Under typical conditions re-growth occurred to only a limited extent, showing that floc breakage was partly irreversible. However, it has recently been found that such behaviour is greatly dependent on solution conditions, especially pH and the presence of certain ions. In some cases very strong aggregates are formed, with almost no breakage at high shear.

Whether or not aggregates re-from after breakage gives valuable information on the interactions between primary particles, but this aspect has been very little studied. Some possible reasons for the observed behaviour will be discussed as well as some of the practical implications.

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O18 Foam stabilization by compositions of surfactants with sodium carboxymethylcellulose

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The combinations between following surfactants sodium dodecylsulfate (NaDDS), ammonium dodecylsulfate (ADDS), sodium dodecyl-2-etoxysulfate (NaDDES), ammonium dodecyl-2-etoxysulfate (ADDES) and cetyltriammoniumchloride (CTACl) as the main foam formers and sodium carboxymethylcellulose (NaCMC) as the stabilizer of foams demonstrates higher foam forming ability than the separate components. This fact can be explained by the formation of complexes and associates between surfactants and NaCMC that leads to the substantial change in the hydrophylic-lipophylic balance and surface activity of NaCMC molecules segments.

The optimum concentration ratios surfactants/NaCMC and the conditions (ionic strength, pH) for obtaining maximum stability of foams were found. On the basis of calculated main parameters - frequency rates, speeds foams syneresis, speed of liquid from foams flow, disperseå, the methods and conditions of foam quality regulation were determined. The foams stabilized by NaCMC were shown to have more lower values of the capillary pressure and multiplicity at higher equilibrium thickness of foam films compared to the foams stabilized by the surfactants.

The foam formation in aqueous solutions of surfactants and their compositions with NaCMC depends on the surfactant nature (counter ion, the presence of oxyethyl groups in molecule). It is shown that the water solutions of sodium etoxyalkylsulphates have the greater foam ability in comparison with the ammonium salts. The values of the layer relaxation time were designed and it was established that the reduction of relaxation time leads to the foams stability growth. Based on values of the formation interphase adsorption layer constants it was found that the limiting stage of the associate surfactants/NàCMC adsorption is the diffusion of molecules to the border liquid - gas. The values of synergetic effect of surface tension decrease were calculated using the surface tension isotherms. The correlation between synergetic decrease of surface tension, surface activity values and parameters of interphase adsorption layers of the surfactants compositions (NaDDS, ADDS, NaDDES, ADDES, CTACl) with NaCMC at the liquid-gas boundary with their foam stabilizing effect was determined. The values of surface activity at the liquid-gas boundary and the parameters of interphase adsorption layer of the surfactant/NaCMC compositions were determined. The high foam stabilizing effectivity of the surfactant/NaCMC compositions may be attributed to the formation of surfactant/NaCMC associates which has higher surface activity than the separate compounds.

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It was found that the sodium carboxymethylcellulose stabilizes the foams surfactants due to the strengthening of the thermodynamic factor owing to the decrease of surface tension upon adsorption of the surface-active associate, the structural mechanical factor owing to the viscosity increasing of aqueous surfactant solution upon addition of polymer, and the electrostatic factor owing to the formation of the dual electrostatic layer in double-side foam film. According to the results of systematic investigations of the foam stabilization by surfactant/NaCMC compositions, we have been found the approach of the optimization of practical significant foam properties and the foam forming compositions for the fire extinguishing and flotation of ores and polluted water purification were proposed.

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Surface potential at metal oxide aqueous interface in the presence of organic adsorbents

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Surface potential (electrostatic potential at the inner plane of the electrical interfacial layer ψ^0) could be measured by single crystal electrodes. Surface potential is dominantly determined by the binding of ionic species directly to the solid surface. These ions are potential determining ions, i.e. H+ and OHf{ ions in the case of metal oxides. Specific adsorption of organic ions changes the surface potential, which in turn affects their state at the interface, i.e. their interfacial activity coefficient. Measurements of surface potential could be used to deduce state of adsorbed organic ionic species at the interface and thus contribute to better understanding of pollution phenomena in the soil. The results with hematite, titania and silica will be presented.

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O20 Sorption of Cu(II) onto North-Eastern French soils: isotherms and spectroscopic studies

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Metals are natural ubiquist constituents of soils. However, heavy metals are also introduced into soils mainly by the application of fertilizers, sewage sludge, and other industrial and urban waste materials. Soils play an important role in the mobility of these metallic cations in the environment. The transport of pollutants, such as heavy metals like copper(II), from their source through soil and water to their final resting place and their impact on plants, animals, and humans along the way depends in detail on the chemical form of the polluting species.

In order to clean up the environment or, in a simpler way, to understand the transfer processes, a scientific approach requires both macroscopic data obtained by sorption isotherms and basic chemical information at the molecular level about contaminants. For example, a remediation strategy depends not just on the concentration of the toxic metal but also on its mobility in soil and water and its ease of uptake by plants, animals, and people, properties that depend on the chemical compounds containing the metal.

In addition to the macroscopic study conducted through batch adsorption experiments, we use complementary spectroscopic techniques to identify coppercontaining compounds in contaminated North-Eastern French soils located in a vineyard region. Indeed, spectroscopic measurements can be used to probe molecular scale surface speciation and sorption mechanisms to complement macroscopic experiments. Electron paramagnetic resonance (EPR) and X-ray absorption spectroscopy (XAS) are complementary techniques. The former gives geometrical information about paramagnetic metallic cations such as copper(II), whereas the latter is generally used to describe the local structure including bond distance, coordination number, and type of near neighbors surrounding a specific element.

In the present study, macroscopic Cu sorption studies as a function of pH and metal concentration are document for five soils with a dramatically different composition. Combined with EPR, extended X-ray absorption fine structure spectroscopy (EXAFS) and X-ray absorption near edge structure spectroscopy (XANES), the previous results allow the characterization of the structure and the stability of the surface complexes formed on soil particles. Therefore, the aims of the present work are (i) to determine Cu complexation mechanisms on soil particles as a function of pH, reaction time, and metal concentration, and (ii) to assess the influence of the solid phase on the first shell coordination environment of sorbed Cu.

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PL4 Microbial Adhesion and Transport in Aquatic Environments

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Understanding the factors governing the adhesion, transport, and fate of microorganisms in subsurface aquatic environments is important in a number of fields, including the protection of groundwater from pathogenic microbes, in-situ bioremediation, riverbank filtration, and land disposal of treated wastewater effluents. A key factor governing microbial mobility in subsurface environments is their adhesion (or deposition) to mineral grains. Recent experimental techniques and models to study microbial adhesion and transport will be described with examples involving bacteria, viruses, and Cryptosporidium oocysts. Emphasis will be placed on the role of microbial surface characteristics and the resulting interactions with mineral surfaces. The successes and failures of current models and theories to depict microbial adhesion and transport behavior will be highlighted and the implications for predicting microbial transport in subsurface environments will be discussed.

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Maghemite nanoparticles: an effective adsorbent for arsenic removal

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Nanoparticles and nanomaterials represent promising tools for environmental protection. Nanoparticles are very attractive because of their important surface area, surface energy and consequently their high reactivity and affinity with adsorbates. They could provide solutions for most of the challenging environmental cleanup problems: water treatment, soil remediation, gas treatment and sensors (pollution monitoring). One of the most important health and environmental problem of these last years is the chronic exposure of millions of people to high rates of arsenic in drinking water (Mexico, Bangladesh, Vietnam.). This large-scale contamination led to a growing interest in minerals, such as iron oxide, which can immobilize and remove arsenic from aqueous solutions. Recently, iron oxide nano-sized particles were used in several fields due to their magnetic properties and their strong affinity with adsorbates (proteins, pollutants.). The aim of this work is to assess the use of nanoparticles as an effective tool for arsenic immobilization and detoxification during water treatment processes.

The iron oxide nanoparticles studied in this work are maghemite nanoparticles (nano-Fe2O3). X-ray diffraction measurement and transmission electron microscopy have shown nanoparticles roughly spherical with a mean diameter of 6 nm. The efficiency of nano-Fe2O3 to immobilize arsenic in solution was quantitatively (ICP-AES) and qualitatively (X-ray Absorption Spectroscopy, XAS) evaluated. Preliminary experiments indicate that the sorption capacity of nano-Fe2O3 is important (1.9 mmol of As/g). XAS led at the As K-edge (ESRF-FAME beamline) revealed that arsenic is strongly adsorbed at the nano-Fe2O3 surface through inner sphere complexes. To further enhance their efficiency in arsenic removal, nano-Fe2O3 were coated with a therapeutically used chelating agent, the meso-2,3-dimercaptosuccinic acid (DMSA: HOOC-CH(SH)-CH(SH)-COOH). XAS experiments led at the Fe K-edge (ELETTRA. Italy) indicated that DMSA forms a strong binding with nano-Fe2O3 surface via its thiolated functions (Fe-S = 2.21 ± 0.02 Å). After the DMSA coating, arsenic is adsorbed on nano-Fe2O3 through the free DMSA _COO- functions and the efficiency of the coated nano-Fe2O3 to remove arsenic is significantly increased (4.9 mmol of As/g). Thus, DMSA coated maghemite nanoparticles could be a very interesting tool to treat arsenic polluted water. One more advantage of such nano-adsorbent is their magnetic properties. The arsenicloaded nanoparticles could be magnetically recovered, regenerated and re-used.

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Functionalized bridged polysilsesquioxanes as adsorbents of volatile organic compounds

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Modern sorption technologies use adsorbents with high porous surfaces, high values of static sorption capacity, selective properties and stability in aggressive environments [1]. The techniques of synthesis of such adsorbents should be simple and easy for reproduction. Furthermore, the methods underlying the synthesis of such materials should give an opportunity for affecting physical, chemical, structure and adsorption properties of the final products. From this point of view bridged polysilsesquioxanes (BPS) are attractive compounds. These hybrid organic-inorganic materials are obtained by means of "mild" solgel method in one-stage process so by proper choice of precursor and conditions of synthesis it is possible to design the considered materials on a molecular level keeping control over their structural-adsorption characteristics.

BPS can be additionally functionalized with different functional groups by cocondensation of structure forming agent (organobis(trialkoksysilane)) with trialkoksysilanes carrying desired functional groups. Functionalized BPS xerogels described in this work were synthesized by such co-condensation of ethylene and phenylene bridged monomers with trialkoksysilanes containing amino- and thiol- groups. Obtained xerogels have relatively high values of specific surface area (500-1000 m2/g) and a high content of functional groups (1-3 mmol/g). A majority of these functional groups (-NH2 and -SH) is located on the surface being accessible to the molecules of adsorbate [2,3]. The main goal of this presentation is to describe two most important factors affecting structure-adsorption characteristics of the xerogels obtained, that is, the porosity and the chemical heterogeneity of the surface. To investigate this subject several adsorption/desorption isotherms were determined: nitrogen, benzene, cyclohexane, hexane, heptane, acetonitryle, acetic acid were adsorbed on a selected xerogels. It was established that the majority of obtained materials have a pores on the border of micro- and mesoporosity; the total volume of the pores is in range $0.5-1.5 \text{ cm}^3/\text{g}$. Results of adsorption measurements of selected organic compounds show that the porosity but also chemistry of the surface plays an important role in the adsorption processes on functionalized BPS xerogels.

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Transport and fate of carbon nanoparticles C60 in aquatic, soil, and organic environments

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Our research is aimed at studying the dispersion and transport of fullerenes C60 in the different kinds of aqueous media encountered in the environment, in order to better understand their becoming and potential impact when wasted. Although fullerenes have always been known as insoluble in water, some procedures have been achieved to disperse fullerenes in water without chemical or structural modification. They consist in a previous step of C60 dispersion in an organic solvent like toluene or THF, allowing the formation of water-stable nanometric clusters. This raises the question of the organisation of water molecules on cluster surface and of the eventual role played by the organic solvent in the dispersion mechanism.

Our work deals with these two open questions, by studying the effect of the solvent used on the surface properties and size of the C60 clusters finally obtained [1], and the affinity of C60 fullerenes with water [2]. Dynamic and static light scattering revealed that all the studied procedures induce the formation of 50-200 nm sized clusters. UV-Vis absorbance spectroscopy revealed that a polar solvent like THF remains chemically bonded to C60 cluster surface, playing the role of surfactant layer assuming stability in water, which may also be responsible of the toxic effects observed in biological administrations. On the opposite case, toluene which is a non polar organic solvent, does not remain adsorbed on C60 surface during dispersion in water, which implies direct hydration of C60 surface and arises the question of the global affinity of C60 for H2O molecules.

A water gas adsorption/desorption isotherm has been realised on a pure C60 fullerite [2]. It confirmed the C60 surface initially hydrophobic with a very weak adsorption of water at low relative pressure. However, at higher relative water gas pressures above 0.7, the C60 surface is irreversibly modified, when two monolayers of water molecules are adsorbed, inducing a more hydrophilic character. This experiment revealed that fullerenes become hydrophilic and hydrated when contact with H2O is forced. This result is of great importance from an environmental point of view, as fullerene dispersion in in 200 nm water-stable clusters can be achieved simply by mechanical stirring. Small angle neutron scattering is going to be used to study the arrangement of the nanometric C60s in such larger clusters in order to determine the mechanism of formation and the size and structure of the smallest particles. Furthermore, the colloidal stability of such a suspension is being studied by static and dynamic light scattering as a function of the organo-mineral composition of the aquatic

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system. For that purpose , different salt and microbial polysaccharides are tested and the respective critical coagulation and flocculation concentrations are determined. The chemical nature of the eventual interactions with macromolecules will be determined by infrared spectroscopy and quantified by adsorption isotherm.

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Colloid-facilitated transport of pollutants under variable redox conditions in a temporary flooded riparian wetland soil. A Microcosm Study

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The role of colloids in facilitating the transport of strongly sorbing pollutants has been demonstrated in oxic soils, but little is known about their importance under variable redox conditions. In riparian wetland soils, temporary flooding may cause periods of microbially-driven soil reduction, followed by abiotic oxidation when O2 supply is restored. During such redox cycles, the mobility of metal pollutants may be affected both directly by altering their chemical speciation as well as indirectly by altering sorbent phases. The objective of our study is to investigate the formation of mobile sorbent phases under variable redox conditions and to evaluate their importance for promoting the release of selected pollutant (As, Cd, Pb) to the river or groundwater during flooding and drainage.

Soil samples were collected from a mining-polluted riparian wetland soil at the river Mulde near Bitterfeld, Germany. A microcosm setup was uniformly packed with air-dried soil (25cm high, 19cm in diameter), flooded for a period of 3 to 5 weeks, and then slowly drained to field capacity. Pore water (including colloids) was extracted at different depths via open-pore (15 m) suction cups into a glovebox-hosted (O2<1ppm) ultrafiltration unit. The concentration and redox speciation of selected redox-sensitive (As(V)/As(III)) and redox-insensitive (Cd(II), Pb(II)) pollutants were monitored in unfiltered and filtered (0.025 m) aliquots. The colloidal fraction was calculated by difference. Colloid composition, size, and electrophoretic mobility were characterized by electron-microscopy and light scattering techniques.

Our results obtained so far demonstrate the formation of Fe and organic matter colloids, and their effect on pollutant dynamics. In the reduced pore water, microbial respiration of Fe(III)-(hydr)oxides led to a dramatic release of Fe(II) (up to 5mM) and associated As (up to 150°M As(III) exceeding the German drinking water standard by 3 orders of magnitude). Intermittently, As(III) was to 20% colloidal, while Cd and Pb were almost completely colloidal. The colloidal phase was found to contain Fe(II)-bearing particles (possibly Fe(II) sulfide minerals) and organic carbon. While Fe(II) particles have likely formed as precipitates from supersaturated pore water, colloidal organic carbon was released from the soil matrix when bearing Fe(III)-(hydr)oxides reductively dissolved. Upon drainage, both colloidal Fe(II) and organic carbon were mobile and carried sorbed or co-precipitated pollutants to the drainage effluent.

Diffusion of Fe(II) toward the oxic-anoxic interface led furthermore to the

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formation of Fe(III)-(hydr)oxide particles in the supernatant water phase. These oxide colloids were rather immobile and deposited on the soil surface during drainage. At the pH 6-7 of the pore water, Fe(III)-(hydr)oxide colloids are positively charged and thus are attracted to the mainly negatively charged soil matrix. In contrast, negatively charged Fe(II) colloids (point of zero-charge of Fe(II) sulfide pH^{2}) are more stable especially in the upper soil layer, where ionic strength remains moderate due to diffusion of dissolved Fe(II) and other ions to the supernatant water phase. Our results therefore point to the

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importance of colloid charge and pore water ionic strength on colloid stability.

Colloidal transport of pesticides in UK aquifers

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Pesticide contamination in groundwater is an increasing problem that poses a significant long term threat to water quality and is of concern for legislators, water utilities and consumers alike. In the dual porosity aquifers common in the UK, movement of pesticides and their metabolites through the unsaturated zone to groundwater is generally considered to be through one of two pathways; a rapid by-pass flow and a slower piston-flow route via the rock matrix. However, the dissolved form or colloidal species in which pesticides move within the water body is poorly understood. Following heavy rainfall, very high peaks in pesticide concentration are often observed in shallow UK aquifers. These concentrations might be well explained by colloidal transport of pesticides.

We have taken groundwaters from two different aquifer types; one reducing and one aerobic. Pesticide and metabolite concentrations were then determined in these groundwater. The aerobic groundwater contained diuron and its metabolites whereas the anaerobic groundwater contained mecoprop, reflecting the differing landuses at the two sites. Colloids were extracted in the laboratory from a large volume of the aerobic groundwater using an ultrafiltration technique which produced fractions from 0.45[°]m to 1kDa. The anaerobic groundwater contained high concentrations of dissolved iron which will precipitate in the ultrafiltration cartridges. This groundwater was therefore passed through a series of filters on site ranging from 5[°]m to 0.1[°]m. Each fraction from both aquifer types was subsequently analysed to determine the concentration of the relevant pesticide and metabolites. Results show the differences between the two aquifer types and the degree to which pesticides and metabolites favour the colloidal fractions isolated in the groundwaters.

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pH-dependent adsorption and desorption of phenol and aniline

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Due to its high affinity to a wide variety of chemicals, AC is very popular in the purification of drinking water, wastewater treatment and emission control. The recognition of the potential hazard of veterinary and human pharmaceuticals in the aquatic environment renewed the concern in the treatment of both wastewaters and drinking water. The increasing consumption of activated carbon also addresses the problem of regeneration, for environmental reasons — disposal of AC loaded with hazardous chemicals should be avoided— and for financial reasons as well.

Aromatic compounds are frequent contaminants in industrial wastewaters. Phenol and its derivatives appear as a consequence of degradation of organic compounds widely used as intermediates in the synthesis of dyes, pesticides, insecticides, explosives, etc. In aqueous solutions, they cause an unpleasant taste and odor already in low concentration. Besides being carcinogenic, in the chlorinating process often employed in the drinking water purification, it reacts with the chlorine and produces carcinogenic (poly)chlorinated compounds. Aniline can be emitted during its production, handling and disposal and as an industrial effluent, or from natural aniline-containing materials, like coal tar. It is potentially toxic due to formation of carcinogenic oxidation products, like azo-compounds. Although several authors reviewed recently the sorption of aromatics from their aquoeus solutions with activated carbons, they unanimously concluded that the specific mechanism of the interaction of many organic compounds on the amphoteric surface of the carbon is still dubious.

In this work the sorption properties of phenol and aniline are systematically studied on the surface of an ash-free microporous activated carbon in a wide pH range (3-11) under oxic conditions. To reveal the acid/base processes occurring on the surface, continuous titration was performed in CO2-free medium. The proton excess isotherms were evaluated by the SAIEUS procedure [1-3] employing a regularization method. Cyclic titration revealed irreversible acid/base response due to multi-step surface reactions involving also the formation of radicals with the oxygen entrapped in the micropores. Combined consecutive redox and acid/base reactions slow down the surface response in the 3-6 and 6-8.5 pH range. Phenol and aniline are adsorbed most strongly in unbuffered conditions, but even then only part of the surface area is utilized. Chemisorption was detected when aromatics may interact in the form of ions.

The Dubinin-Astakhov (DA) adsorption-isotherm equation was used to evaluate

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the parameters characterizing the adsorption. Adsorption energy distribution functions have been calculated by using algorithm INTEG based on the regularization method. Analysis of distribution functions for activated carbons provides significant comparative information about their energetic heterogeneity. Besides, a comparison of the resulting energies obtained from the distributions can be made with enthalpy data.

Aggregation and deposition kinetics of fullerene nanoparticles in aquatic environments.

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Since the discovery of Buckminsterfullerene C60 in 1985, it has drawn widespread attention to its diverse potential applications in the fields of electronics, optical, and biomedical engineering. Fullerene has unique chemical properties, likely to be related to its spherical cage-like molecular structure. With the development of a method for fullerene mass production, it is estimated that fullerene production can reach about 10 tons per year by 2007. As fullerene-based products are mass-produced and subsequently used by industries and consumers, it is inevitable that fullerene may end up in natural and engineered aquatic systems as pollutants. Since fullerene can be highly reactive, fullerene pollution may have environmental and ecological impacts. Moreover, studies have indicated that fullerene is toxic to microbes and fish, raising concern about the adverse human health effects it \max cause. Under aqueous conditions, hydrophobic fullerene molecules bind strongly to one another forming stable fullerene nanoparticles. Thus, it is likely that fullerene will exist in the form of nanoparticles when released into natural waters. The fate and transport of these nanoparticles are dependent on their deposition behavior onto mineral surfaces and their aggregation behavior. This study investigates the inter-relationship between the deposition rates of fullerene nanoparticles onto quartz surface and their aggregation behavior in the presence of common monovalent and divalent electrolytes.

Fullerene nanoparticles are synthesized by transferring fullerene from toluene into water phase through sonication of fullerene/toluene/water mixture. The suspension is filtered through a 0.2 micrometer filter, resulting in polydisperse spherical nanoparticles with diameters mostly ranging from 30 to 100 nm, as observed by TEM.

Deposition studies are conducted with the piezoelectric quartz crystal microbalance (QCM). Quartz crystals are employed as the model mineral surface. Fullerene nanoparticle suspension in the presence of sodium or calcium chloride is directed across the quartz surface under constant flowrate and particle concentration. The electrolyte concentrations are varied to investigate their influence on the deposition kinetics of the nanoparticles onto quartz surface. Results demonstrate that at low to moderate salt concentrations, increases in ionic strength lead to corresponding increases in fullerene deposition rates, due to charge shielding between the fullerene nanoparticles and quartz surface. Under such conditions, the deposition rates remain constant within the period of deposition (about 1 hour), indicating deposition at the low surface coverage regime. However, further increases in electrolyte concentrations resulted in decreasing deposition rates with time, with the initial deposition rate being lower than under favorable (non-repulsive) conditions. Dynamic light

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scattering shows that at the higher electrolyte concentrations, the nanoparticles undergo significant aggregation within the experimental time frame. At low electrolyte concentrations, fullerene primary particles undergo deposition onto the quartz surface. However, at higher electrolyte concentrations, the energy barrier to aggregation between the negatively-charged nanoparticles deceases, leading to simultaneous aggregation and deposition. As time progresses, larger aggregates are formed, resulting in decreasing deposition rates due to lower convective-diffusive transport toward the quartz surface. Flushing the system with deionized water after the deposition experiments does not cause observable release, indicating that particle deposition is irreversible.

Cation bridging of colloids as indicated by multi-stage tangential ultrafiltration

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There are various indications in the literature suggesting that colloids may act as a main carrier for the translocation of heavy metals in soils. Liming is used as a common method to remediate Pb-contaminated shooting range sites. However, the effect of liming on the mobility of colloids is not clear at present. The liming-induced increase in pH is assumed to mobilise colloids, while the addition of Ca2+ induces the flocculation of colloids

We tested the hypothesis that (1) increasing pH causes the mobilisation of colloidal Pb, As and Sb, (2) the addition of Ca2+ reduces this pH-effect and (3) both change in pH and valency of counterion impact on the elemental composition and size distribution of colloids.

We conducted batch experiments using soil samples (pH 5) from a former shooting range site. The pH was increased to 6.5 by adding either KOH or Ca(OH)2. Differences in ionic strength of the treatments were compensated by adding KNO3-solution. A control batch was shaken with KNO3-solution. Multi-stage tangential ultrafiltration was used to separate colloids in suspension into different size fractions following shaking and filtration over a 1.2 `m membrane. The filtered suspensions of the individual size fractions were analysed for Pb, As, Sb, Fe, Mn and Corg.

The control batch showed approx. 25 % colloidal Corg, whereas all other elements predominantly remained in the dissolved fraction (< 100 kDa). Increasing the pH with KOH resulted in both a high release of dissolved organic matter by the soil matrix and a dramatic increase in dissolved and colloidal Pb concentrations. Colloidal As, Corg, Fe, Mn and Pb were all found in the smaller size fraction between 100 kDa and 220 nm. Increasing the pH with Ca(OH)2 revealed a completely different colloidal size distribution. Colloidal Pb mainly occurred in the size fractions between 220 and 1200 nm. Total As and dissolved organic carbon concentrations in the suspensions dropped significantly.

Whereas the dispersion of sesquioxides is enhanced by increasing the pH with KOH, it is suppressed by the addition of Ca(OH)2. We conclude from our result that bridging effects of divalent cations cause the flocculation of mineral colloids, the main carrier of colloidal As and Sb of the studied soil. In addition Ca-bridging induces the formation of large organic colloids, which may adsorb Pb.

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The obtained data is to be compared with results to be gained by means of (ultra)filtration and complemented by the characterization of the detected colloidal precipitates by scanning electron microscopy.

Transport of metabolically active microorganisms in unsaturated porous media

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The transport and mobility of bacteria through porous media under unsaturated conditions is poorly understood. This study sought to investigate: (i) the influence of matrix saturation; (ii) the role of the bacteria surface characteristics; (iii) the effect of matrix grain size; (iv) the influence of substrate; and (v) the role of bacterial surface protein. Experiments were conducted in unsaturated porous medium (quartz sand) using two strains of hydrophobic differing bacteria, Deinococcus radiodurans and Rhodococcus rhodochrous. The effluent concentration was measured continuously during the experiment, whereas the retention profile was obtained afterwards by careful segmentation of the packed column. Fluorescence microscopy was used to account for the effluent concentration and spatial distribution within the column packing.

The decrease of the water content led to a higher retention of bacteria close to the column inlet for bacteria in the stationary phase. This effect was more pronounced for hydrophobic bacteria. In the active (log) phase, bacteria retention increased. Also, a continuous cell release in the outflow was observed after the breakthrough curve, due to cell division. The growing cells showed an increasing hydrophobicity during the log phase, because of changes in amount and type of protein present on the bacteria surface. Enzymatic treated bacteria without protein showed less attachment to the sand surface. The observed data was modelled using a modified HYDRUS computer code as well as the Dual Deposition Mode model to further elucidate transport mechanisms of metabolically active bacteria.

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Metastable equilibrium adsorption (MEA) theory: thermodynamic, sprectroscopic and quantum chemical development

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MEA theory proposes a fundamental deficiency in the existing theoretical foundation of adsorption thermodynamics that adsorption density &Gamma (mole/m2) has been incorrectly used as a state variable in the past. When &Gamma is not treated as a state variable, classical thermodynamic adsorption principles will have to be re-examined so that equilibrium adsorption constants will be fundamentally affected by the kinetics/reversibility of adsorption processes. This implies that previously measured equilibrium adsorption data may show a lack of consistency, making the use or comparison of the data problematic. Both spectroscopic methods of EXAFS and XANES and theoretical methods of quantum-1964) pr chemical calculation were developed to study metastable adsorption at the molecular level. The results also explained the thermodynamic reason for the anomalous phenomenon of particle concentration effect. Applications of MEA theory to the modeling of phosphorus cycling in Nile River-Eastern Mediterranean Sea (p oduced a P flux 60% higher than conventional thermodynamic predictions.

P.S. This presentation will be a summary of the development of MEA theory based on the following publications

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- 4. Ma, ZC, Pan, G. et al., A thermodynamic study on the relationship between metastable equilibrium adsorption states and the metastableequilibrium coefficient of surface adsorption reactions, CHEMICAL JOURNAL OF CHINESE UNIVERSITIES, 2005, 26 (3): 476-479
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PL5

Fundamental problems of soil decontamination by application of an electric field

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Remediation of industrial soils contaminated from radionuclides, heavy metals and other pollutants is a very important and complicated problem. Special attention deserves the process of soil recovering by application of an electric field. The method is based on the mass transfer of polluting substances under the action of the external electrical field, together with their subsequent extraction from the cathode chamber. Transfer of soil components can be achieved by electrophoresis, electro-osmosis and diffusion, osmotic and convective movement of liquid, and depends on many factors: soil chemistry and structure, desorption, ion exchange, polarization of soil particles and electrodes, electrokinetic mobility of pollutants etc., which affect the efficacy of the decontamination processes. Thus, a comprehensive approach to the detailed analysis of all proceeding processes and the development of new technological ideas is a matter of paramount importance.

Unfortunately, according to numerous investigations, the application of an electric field in a wide range of voltage or current density shows rather low efficiency and/or rate of decontamination. It is astonishing that the strongest negative factor of soil remediation in an electric field is an electric field itself. An electrical current is always accompanied by the electrolysis of water on electrodes, which leads to the change of soil pH, creation of inhomogeneous local surface potential and conductivity of soil, inhomogeneous local solubility, as well as desorption and mobility of pollutants due to the field. The most negative role is played by alkalinity of soil near the cathode, where a considerable fraction of contaminating ions lose their solubility.

Prevention of the negative influence of soil alkalinity can be achieved in a few ways: introduction of complexing agents, wetting of the soil by acid solutions, use of ion-exchange membranes, and conditioning of the catholyte pH. Each of these methods has some disadvantages. Introduction of complexing agents very often successfully averts the negative influence of an alkalinity, but the created complexes have lower mobility in the electric field in comparison with that of the contaminating ions. The wetting of soil by acids and the conditioning of catholyte pH, as well as the use of complexing agents need rather high amount of reagents and in fact bring about a secondary pollution of soil. Allocation of soil between cation- and anion-exchange membranes prevents the movement of hydroxyl ions into the soil. However, water splitting caused by polarization of membranes and/or creation of a bipolar contact between membranes and soil

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create ion fluxes similar to those produced on the electrodes. Therefore, the careful optimization of the known methods and the development of new ways of pH regulation is one of the most important problems of soil remediation worthy of special attention.

We have conducted theoretical analysis of all processes during soil remediation under galvano- and potentio-static regimes, as well as under pulsed regime. In addition, our experimental investigations gave an opportunity to develop the scheme of pH, ion flux and electrokinetic potential regulation, leading to an acceleration and enhancement of soil decontamination from charged and noncharged pollutants. The obtained experimental data, concerning the remediation of model and real soils polluted by different heavy metals and radionuclides, as well as non-charged pollutants, have shown that a high degree of remediation can be reached.

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Ferroxane nanoparticles used for the fabrication of iron oxide ultrafiltration membranes: a new route for the synthesis of catalytic membranes?

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Ferroxane nanoparticles, obtained from reaction of lepidocrocite (FeOOH) and acetic acid at room temperature, and the selection of nanoparticles of lepidocrocite were applied to the fabrication of ceramic membranes. The size of the nanoparticles and the kinetics of the reaction were investigated. The effect of the acetic acid on the formation of ferroxane was investigated Ferroxane and lepidocrocite derived membranes were prepared and characterized by nitrogen adsorption/desorption isotherms, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Permeability and molecular weight cut off measurements were conducted on asymmetric ferroxane-derived membranes. The average pore size was determined to be 24.11 nm and the BET surface area was $75.6m^2/g$. Permeability was measured for membranes with one, two, and three coatings, to determine the effect of thickness of the ferroxane layer on the membrane hydraulic resistance. The MWCO of the ferroxane-derived membranes was 150,000 Da, which falls in the ultra-filtration range. The membranes exhibit a high affinity for chromate. This property let us think that it is now possible using nanoparticles to synthesize catalytic membranes.

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Solidification of liquid hydrocarbons in water by lithium carboxylate crystal fiber and the properties of the solidified aggregates.

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In parallel with the development of chemical industries in the 20th century, in many places on the earth, water, air and soil have been polluted by many kinds of hydrocarbon oils and other organic substances. For remediation of oil polluted water, many kinds of inorganic materials, organic polymers, and surfactants have been developed and used. Each material is useful for each purpose, to catch and detect precisely very small concentrations of oils in water. However, by using these already utilized materials and methods, it is difficult to catch and recover much amounts of oils dissolved or dispersed in water. For example, active charcoal fiber can catch organic materials in water effectively, but the total amount of oil to be caught by active charcoal is at most less than 1 by weight compared with active charcoal used. We have already reported that very thin and long fiber crystal of sodium- or lithium carboxylates can catch more than 5 to 10 times (by weight) of liquid hydrocarbons and halogenated hydrocarbons dispersed in water, and apparently solidify to make gigantic aggregates (IAP2002 and IAP2004). In this paper, solidifying procedure of liquid hydrocarbons and properties of the resultant aggregates will be reported in more detail.

Very thin and long lithium dodecanoate fiber crystal, C11H23COOLi, was synthesized from n-dodecanoic acid and LiOH.H2O in aqueous solvent at 100 degree C under atmospheric pressure. The fiber crystal was washed and dried under vacuum, and then completely dried fiber crystal was obtained. It was more than 97% pure by elementary analysis. By SEM observation, it was clear that one fiber bundle was composed of many thinner fibers, less than 0.1 micrometer diameter and more than 10 micrometer long. By DSC, TGA, XRD, and C-13 NMR analysis, it became clear that crystal structure and themal properties of fiber crystal of lithium dodecanoate (F12Li) were much different from scaly crystal of lithium dodecanoate (C12Li), which will be reported elsewhere.

As a typical model of solidification, F12Li and n-tetradecane (1:2 by weight) were mixed well to become apparently solidified gigantic aggregate, and the aggregate was analyzed by DSC, TGA and C13-NMR. In the aggregate at room temperature, n-tetradecane was exactly the same liquid state as free n-tetradecane, and F12Li was also the same manner in both free crystal and in the aggregate. These results show that only intermolecular van der Waals force between alkyl chains of F12Li and n-tetradecane is the origin of the formation of aggregate.

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Electro-osmosis remediation kinetics of heavy metal and radionuclide contaminated wastes and soils

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To a large extent, effectiveness of electrokinetic techniques for decontamination of metal polluted slurries and soils is determined by the chemical form of contaminants in the environment. Under an electric field the easiest removing from the disperse systems is for such radionuclides or heavy metals that are in pore solution in a free ionic state. At the same time, if there are rather strong adsorption bonds between contaminating ions and active centres of the solid phase, their removing will be extremely complicated.

Among the most important natural minerals are clays that are highly dispersed and therefore, substantially determine colloid properties of soils. It is typical for clay minerals to form strong surface complexes with radionuclides and heavy metals. In contrast to the classic theory of specific adsorption in Stern's electrical double layer (EDL) according to a generalized model EDL that includes the idea of the features of surface complex formation, metal ions that are part of these complexes complete the crystal structure of solid phases, thus determining their potential Ψ . Rather mobile outer-sphere complexes form Stern's layer up to the outer Helmholz plane and the diffusion part of an EDL.

It is known that a typical feature of an electro-osmotic transport compared to a filtration is the emergence of considerable velocity gradients in the immediate proximity of the surface – inside of an EDL. Therefore, the findings of traditional sorption experiments (in statics and dynamics) cannot be completely ascribed to sorption processes that occur during electrokinetic soil remediation, but enable us to characterize their major physicochemical properties.

The usual approach to the consideration of the electroremediation kinetics is based on three main transport mechanisms: electro-osmotic flow which is controlled by the coefficient of electroosmotic permeability of the soil; ion electromigration which is modified in order to account for an effective soil porosity and tortuosity and a mass transport due to hydraulic gradients.

The new way to look at the kinetics of metals removing in disperse systems is developed in view of sorption-desorption processes in layers adjacent to the surface of the mineral particles. The proposed model represent the attempt to include into consideration the principal difference between fluid flow in pores under an hydraulic gradient and an electric field.

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The experimental results, which were received on model kaolinite systems contaminated with copper and uranium ions, show good agreement with theoretically calculated values, but in more complicated cases as real natural soils the agreement is not so good and further development of proposed approach is needed.

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Electric field behavior in the course of an electroremediation of a soil contaminated by lead

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Soil contamination became a concerned problem giving rise to many laboratory studies in recent years. It is due to the fact that various phenomena and numerous factors can intervene as pollutants provoking serious dangers to the human health. Heavy metals are generated from the factors which are the most difficult to eliminate. Despite the fact that processes adapted to organic compounds are varied, those that treat heavy metals are underdeveloped. Electrokinetic soil remediation is one of in situ process that has been recently developed. It is also called either electrodialytic or electroosmosis, and it combines the technique of electrodialysis with electromigration of ions in the contaminated soil. However, the physico-chemical soil-contaminant interactions that occur simultaneously during the process may limit the efficiency of contaminant transport. In effect, in many cases, the water dissociation near the electrodes produces both H+ and OH- ions. The increase of hydroxyl production can give rise to hydroxides precipitates in some cases. To prevent this phenomenon and enhance the decontamination organic acid can be added near the cathode to neutralize the OH- produced by water dissociation and complexing agent as EDTA can also be used to facilitate the metal desorption from the contaminated soil. In this work, the electrokinetic remediation of an Algerian soil contaminated by lead is studied. The contaminant results from a battery manufactory located at 12 km in the east of Algiers near an agricultural area. Two routes have been examined to enhance the electrokinetic process: the use of acetic acid and disodium salt of ethylendiaminetetraacetic acid. It has been noticed that the behaviour of the electric field gives rise to an explanation of the phenomena which take place inside the cell used. Thus, Both Voltage and electric current measurements are performed to show the electric field strength variation inside the soil for each case studied. Electrokinetic tests were carried out in a cylindrical Teflon cell. The central compartment (length = 12.5 cm, inner diameter = 2.5 cm) containing the specimen is separated from cathodic and anodic sides by a filter paper (Whatman N°5) inserted between a grid of rigid nylon (mesh size = 2mm). The circulation of the catholyte and the analyte 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 metallic electrodes (platinum - coated titanium sheets). A weighed amount $(90.0 \pm 2.0g)$ of the soil is put in the central compartment and saturated with deionized water. The applied voltage is delivered by a power supply (Consort E802) and maintained constant in all the runs at a value of 15.5 V corresponding to an

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electric field strength of 1 V.cm-1. The voltage across the cell is measured by means of platinum wire (diameter = 1mm) connected to a multimeter and

Electric current, voltage and pH from a distance of the anode were followed as a function of time for each case studied. Results obtained have shown that electric field appears to be constant during all the experiment contrarily of those where pure water is used. All variation of the voltage can be linked to physical or chemical modification inside the specimen treated giving rise to interesting

inserted at a depth of 3 mm of the soil, using the cathode as a reference.

information to optimise the process.

A new concept in titanium dioxide photocatalyst for water purification

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Much work is being currently devoted to the development of solar processes to water decontamination. Among solar procedures, heterogeneous photocatalysis (HP) holds promise as a good candidate to develop technology beyond the laboratory scale. However, this promise has not been realized until now, and several problems must be solved before this is achieved. Among the problems, the natural fluctuations in solar radiation preclude the use of continuous processes that depend on a reliable light source. Also, the efficiency of HP in water is known to be lower than in the gas phase.

A possible way out of these problems is the development of a two-step process, by separating the removal stage from the HP stage, and carrying out the latter one in moist air, rather than in water. For this end, a sturdy, high capacity heterogeneous catalyst is required that may also function as a filter to remove the pollutant in a separation stage. The present paper describes the synthesis of mesoporous TiO2 powders, in the anatase variety, in the laboratory scale. The aerosol synthetic procedure is presented, together with the characterization of the material by Scanning Electron Microscopy. Transmission Electron Microscopy, in the Dark Field mode was used to measure the degree of crystallinity, and Small Angle X-ray Diffraction was used to probe the ordering of the material. Pore size was also measured, and pore accessibility was determined using FTIT-ATR in the presence of various adsorbates. The adsorption capacity of a model compound for natural organic matter, gallic acid, was measured, together with the rate of its photocatalytic mineralization in water. The photolytic destruction of gallic acid in wet air has not yet been tested.

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O36 Particle-bacteria interactions in a drinking water supply system

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The drinking water supplied to more than 3 million people in Melbourne, Australia, is sourced from fully protected catchments of the upper Yarra River. The main quality indicator used to manage these source waters is turbidity. This is due not only to the health and aesthetic issues associated with the particles themselves, but also to reports that particle-associated bacteria are more resistant to disinfection than those that are free-living. This is especially important for the local system, which supplies water that is disinfected, but unfiltered. Little is known, however, about how the properties of bacteriaparticle interactions influence resistance.

The aim of the current study, therefore, was to better understand particleassociated bacteria within Melbourne's drinking water supply system. To this. column-based deposition experiments, as well as the achieve were characterisation of hydrophobicity and electrokinetic properties. undertaken. Both environmental (Aeromonas hydrophila, Serratia marcesens, Pseudomonas aeruginosa) and laboratory (Escherichia coli) bacterial strains were studied. For the particles, heterogeneous soil samples, as well as separated fractions of sand, fine sand, silt, and clay were used. In addition, goethite, and goethite with humic acid adsorbed to its surface, was employed as a model particle.

The bacterial strains tested were all found to adhere more readily to substrata of greater hydrophobicity, whilst bacterial surface hydrophobicity was also found to be positively correlated with adhesion. Parameters including deposition rate were also determined, and interaction energy modelling undertaken using the DLVO theory. The results obtained have thus allowed us to quantify (on a macro-scale) the extent to which bacteria and particles from the local drinking water supply system are likely to interact in the environment. This data will be used, in conjunction with further studies, to investigate whether the degree to which bacteria are able to adhere to particles influences their resistance to chlorination.

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Binding of variable charge colloids, like humics to charged mineral surfaces, and its effect on ion adsorption

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There is a big conceptual difference between the formulation of the binding behavior of small well defined ions like phosphate to mineral particles and the binding of less well defined nano size variable charge particles like humics. For a small well defined ion only a few species are of relevance (HPO4, H2PO4, (SO)2PO2, (SO)2POOH, etc.). The number of possible states that the nano particle can have for a certain pH both in the solution phase and in the adsorbed phase is extreme, the more so the more reactive groups there are per nano particle. Ion binding models like NICA-Donnan calculate the average state of the molecules/particle for given conditions. A challenge is to link the concentration of the particles free in solution to the concentration of the particles near the surface of a charged mineral. This is a challenge because the chemical state of the particles is not the same in the solution phase and in the adsorbed state. The degree of protonation of the particles is a function of the local electrostatic potential, which is different for the non-adsorbed particles in the solution phase and the particles in the adsorbed phase. The challenge is to be able to calculate the free energy difference between the humic particles (or other variable charge particles like proteins) in their respective environments. This problem has recently been solved (Weng, van Riemsdijk and Hiemstra 2006 Langmuir 22:389-397) and an analytical equation has been obtained for the NICA model that calculates the difference in free energy between different chemical states of the humics. The analytical solution is possible due to the beauty of the analytical NICA equation itself. This approach < which is called ADAPT (ADsorption adAPTation) has been incorporated in the LCD (Ligand and Charge Distribution) model. The new approach will be discussed and it will be shown how it can be extended to describe the binding of FA (fulvic acid) and HA (humic acid) to a mineral like goethite. The adsorbed humics can influence the binding of anions like phosphate and arsenate via the effect on the potential near the mineral particle, via competition for reactive surface sites and via sterical hindrance due to the size of the adsorbed humics. The competition will be sensitive to the calculated structure of the electrostatic potential near the interface. In principle the effect of the presence of humics on the binding of small anions can be predicted from the model using the parameters from the binary systems. The cation-humic-mineral interaction is more complex, because the cations can bind directly to the mineral surface, they can bind to the humic adsorbed to the mineral via an ion bridge or they can bind to the adsorbed humic at sites that are orientated towards the solution phase. The new model approach can also be used to interpret this complex system.

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Removal of lead (II) from kaolinite of Çanakkale (Turkey) by using electrokinetic remediation technology

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: Electrokinetics is defined as the motion of charged ions between two electrodes on which electrical field is applied. This phenomenon can be applied to the many fields related to civil and environmental engineering such as consolidation and stabilization of soils, dewatering in construction sites, decontamination of pollutants (called as electrokinetic remediation), and injection of chemical agents to soil. Recently, several laboratory and field scale works represent that electrokinetic remediation technologies are used efficiently to remediate soils polluted by heavy metals.

In our experimental works, calculated concentrations of Pb(NO3) solution were added to 1,5 kg sample, in which the soils lead concentration was converted to about 4000 mg/kg. The soil contaminant mixture was manually mixed. Then, it was allowed to equilibrate for 48 hours. Prepared slurry was transferred into specimen cylinder. After that, specimen cylinder was assembled in electrokinetic extraction cell. The electrokinetic remediation was conducted for 10 Volts.

In this paper, the removal of lead (II) from kaolinite taken Çanakkale (Turkey) region under various process conditions is investigated. In the experimental works, it is observed that Çanakkale kaolinite consists of approximately 40% kaolinite, %60 quartz and insignificant amount of (>5%) allunite minerals. It is classified as CL type soils according to USBR Soil Classification.

Electrokinetic remediation tests in this study were shown that significant precipitation reactions were taken place on the regions closed to the cathode for the experiments on which the enhancement was not applied. By adding 0,5 molar acetic acid to cathode compartment, these reactions were hindered. For the 10 volts potential application and 473 hour treatment time, the lead (II) removal between 50%-85% was reached up to 70% of the normalized distance.

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Methanogenic activity under different nickel forms

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Anaerobic wastewater treatment is a common technology for wastewater cleaning. Upflow anaerobic sludge bed (UASB) bioreactors have been used successfully for more than 25 years to treat industrial wastewaters with a high organic matter concentration. Granules that develop in UASB bioreactors are dense conglomerates. The granules consist of microorganisms, their microbial produced components like extracellular polymeric substances (EPS) and biominerals (iron sulphide, calcium carbonate . . .) (van Hullebusch et al., 2006).

Essential metals like nickel, cobalt or iron play an important role in the metabolism of anaerobic microorganisms. Low concentrations of these nutrients can cause a limitation of microbial activity of the bioreactor. In these cases, the addition of the required nutrient is needed to achieve a proper organic matter removal (Zandvoort et al., 2003).

The bioavailability of a certain metal in biofilms like granular sludge is managed by the chemical speciation and by physical processes too (e.g. adsorption). The chemical form that the metal is present and the biofilm characteristics lead the metal bioavailability. However, it is usually assumed that the metal species that better correlates bioavailability and metal concentration is the free metal ion concentration in the liquid phase (Weng et al., 2005).

In order to study the bioavailability of nickel in an aerobic granular sludge, a UASB reactor-treating methanol was run during 130 days without nickel in the feeding. Methanogenic granular sludge limited on nickel was achieved.

By means of batch tests, the apparent affinity constant (K m) and specific maximum methanogenic activity (rmax) for nickel was calculated for nickel chloride and for nickel bound to EDTA (Table 1). The initial free nickel concentration was calculated in the liquid media by equilibrium speciation model (MINTEQA2). The initial free nickel concentration in the medium with nickel chloride was around 28% and for the medium with nickel bound to EDTA was less than 0.1%.

Table	1.	Kinetic	parameters
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	Nickel Chloride	Nickel bound to EDTA
$r_{max} (g CH_4-COD/g VSS*d)$	2.51	3.17
$ m K_m~(~\mu~M)$	0.128	0.225

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Both K_m values show that the concentration needed to overcome the limitation on nickel is quite low, 0.12 μ M and 0.22 μ M of Ni²⁺, for nickel chloride and nickel bound to EDTA, respectively. The percentage of free metal concentration is 0.04 μ M and 0.002 μ M of Ni²⁺, for nickel chloride and nickel bound to EDTA, respectively. The r_{max} of the medium with nickel bound to EDTA is 20% higher than the medium with nickel chloride. These differences are not in agreement with the assumption that the free metal species is the bioavailable one in the biofilm system.

The different nickel species that are formed during the batch tests could overcome the metal bioavailability. For example sulphide ions, which are always present in granular sludge, could react easier with nickel chloride than with nickel bound to EDTA to form nickel sulphide. The latter is a strongly bound species, which makes the nickel not available for the methanogens. In this way, the nickel bound to EDTA could be more available for the methanogenic cell that leads to higher methanogenic activities.

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Assessment methodologies for Copper and Zinc behaviour in a neutral synthetic soil: pH influence.

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The assessment of metallic pollutants mobility in soil is the topic of a large number of contributions in various fields: hydrogeology, standardization and regulation, health and risk assessment, polluted sites and soil remediation processes,... Our paper analyses the mobility of two metallic pollutants, Copper and Zinc in a porous soil. We applied methods currently used in chemical engineering.

A synthetic soil, composed of sand, calcium carbonate, kaolin, Fe oxide and peat was constituted, based on the European classification of soils (Kuhnt, 1990) and on the ISO guidelines for elaboration of biological test supports (ISO 11268-1, 1993).

The main physical and chemical characterization of the soil and of its components were carried out in order to determine, for example, particle size distribution, buffering capacity in relation to acid input flow, ion exchange capacity, phenol/carboxylic groups repartition or global acidic behavior of peat. Equilibrium data for Cu and Zn in soil were determined in batch reactor and respectively kinetic data in closed micro column systems. Experiments pointed out the major part played by the pH control.

Continuous set-up were carried out in three scale-up laboratory columns (two diameters and three heights of soil layer). The used feed solutions were monoor bi-metallic at constant ionic force 0.1M and constant pH in a range from 4.8 to 6.8. Very reproducible column preparation and testing rules were established. The obtained breakthrough curves were been obtained from long term experiments: volumes of input solutions exceeded 3000 times the open porosity of the systems. Globally, the systems seemed to reach steady state with respect to pollutants concentration (for all columns output/input concentrations=1) but not with respect to output/input pH. Axial local analysis of pollutants retention (total content and selective extractions to differentiate the different sorption mechanisms) in the columns showed concentration gradients. They are linked to different parameters like the intrinsic chemical characteristics of the metallic species, the pH of the input solutions, the behavior of the porous medium,. governing the local pH and therefore metallic species distribution in the column. In fact, pH results from the physico-chemical and transport processes of the reactive metallic species in the liquid phase of the synthetic soil disposed in the columns. For the same global response in term of pollutants output/input concentration, the systems have pointed out various local responses that can be linked to different pH intensities and axial gradients.

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Surfactants on soil water transport to assess remediation criteria

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The subsurface environment has been traditionally a receiver of physical and chemical pollutants increasing environmental degradation. Particularly for chemicals, to effectively reduce contamination problems and mitigate contamination threats it is necessary to control variables governing transport. Therefore, knowledge on the rate at which water and chemicals move through the soil is critical for estimating the rate at which pollutants move into the groundwater. Surfactants are among the most used product for soil remediation providing particular characteristics to the soil solution.

The fluid transport through soils is governed by soil physical and hydraulic properties as well as by fluid characteristics. By adding surfactants it is possible to modify surface tension and therefore modify the hydro-physical behaviour of the medium; and, as a consequence it is possible to control the fate of pollutants in the soil-water system. Changes in soil-water medium properties (hydraulic conductivity, sorptivity, effective suction at the wetting front, solid-liquid contact angle) with the application of surfactants with different chemical structure and characteristics were compared with water (control). Experiments were carried out in soil columns (15 cm length and 2.5 cm i.d. made of methacrylate) flushed with solutions at constant pressure head. The experimental design allows to obtain infiltration curves for accurate estimates of soil parameters avoiding the natural soil variability.

ults show that cationic and anionic surfactants have significant effect on soil properties whereas non-ionic ones did not reveal significant impact. In general, surfactants at concentration above its cmc (critical micelar concentration) increase soil water retention. The interacting mechanisms of the surfactants with the soil particles are strongly depend on pH conditions and soil organic matter content. Electrostatic adsorption, exchange mechanisms and co-adsorption processes can occur either independently or combined, and soil particle behaviour can change from hydrophilic to hydrophobic or vice versa reducing environmental impact.

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Kinetics of pollutants adsorption at solid/solution interfaces: a search for the theoretical background of the empirical pseudo first and second-order kinetic equations

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Adsorption at solid/solution interfaces is a process of a crucial importance for life on our planet and a variety of technologies used in environmental protection. So, it is to be strongly emphasized that the kinetics of these adsorption processes is at least as much essential as their features at equilibrium. Meanwhile the general understanding of and description kinetics itstheoretical are \mathbf{far} this behind the understanding and theoretical description adsorption of equilibria in these systems. For instance, the empirical kinetic equation proposed by Lagergren at the end of the 19th century is still the most frequently applied kinetic equation even now at the beginning of the 21rst century, theoretical background is still unclear. The whereas itsclassical kinetic theories failed to explain its origin. Here, we are going to propose a first theoretical development of the kinetic Lagergren equation based on the Statistical Rate Theory of Interfacial Transport.

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Kinetic analysis of bioremediation of crude oil

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Investigations into the existing bioremediation approaches adopted by many stakeholders especially the oil producing company is the Niger Delta region of Nigeria in order to enhance better remediation process was done.

The study was designed to use mathematical expressions to describe the rate bacterial growth in a bioremediation process and also for the translation of qualitative observations into process parameters for the design and operation of the process. For this purpose, data were obtained from existing literature and analyzed using statistical methods and reactor constants calculated using kinetic models.

The data did not fit very well into the Monods kinetic model, perhaps because most of the verification data were obtained under conditions which violated the assumption underlying Monods model. However, results showed generally that the use of bacteria and fungi are necessary for crude oil degradation, and high nutrient concentration also enhances biodegrading.

The result also showed the need for modeling bioremediation process.

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Surface characterisation of fungi and its implications to metal ion adsorption

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Heavy metal pollution of water ways via industrial activities has the potential to have considerable impact on the environment. Specifically, heavy metals tend to accumulate through the food chain, leading to serious environmental and public health problems. Therefore technologies that allow efficient and economic removal of metal contaminates are highly desirable. Biological substrates provide the basis of one such technology and have been shown to remove aqueous heavy metals from effluent streams. Many biological substrates have been studied ranging from fungi, bacteria, seaweed and leaves. Fungal species in particular, have shown promise as effective, efficient and economic adsorbents, comparable to currently used inorganic substrates.

Metal removal by biological substrates occurs through a process known as biosorption, which is considered complex, often involving multiple mechanisms such as ion exchange, complex formation and/or precipitation. While the suitability of various substrates has been extensively studied, elucidation of the mechanisms involved has yet to be as thoroughly examined.

This study examined three inactive (dead) fungal substrates (Mucor rouxii, Pycnoporus cinnabarinus and Rhizopus stolonifer) for their potential to remove a range of divalent aqueous heavy metals from solution as a function of pH. It was found that Mucor rouxii demonstrated substantially greater adsorption efficiency than the other two fungi for all metals studied (Cd(II), Cu(II), Mg(II), Pb(II), Ni(II) and Zn(II)). Kinetic studies of Cu(II) adsorption show that the biosorption step is a relatively fast step with the majority of adsorption occurring within the first minute.

The mechanisms responsible for biosorption were studied through a range of surface characterisation techniques including, analysis of the chemical structure of the substrates (via X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR)), electrophoretic mobility studies and modelling of surface charge titration data. Spectroscopic studies established the importance of both carboxyl and amine functionality, a finding also supported by the surface charge modelling of the three fungi. Adsorption efficiency appears to be directly correlated to the amount of these functional groups present M. rouxii, in particularly, was established as a suitable candidate for removal of heavy metals from solution and worthy of consideration as a biological adsorbent.

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Enhanced biotreatment of selenium via specialized bacterial groups

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The importance of selenium in environmental research is related to the fact that it shows only a marginal line between the nutritious requirement (as an essential element) and toxic effects upon exposure. In order to treat metal contaminated wastewaters, different physical/chemical and biological processes have been investigated. Biologically mediated metal reduction can be used in order to convert selenate and selenite to elemental selenium.

Selenium conversions are influenced by sulphate, but literature gives contradictory information about these influences. Due to similarities in chemical properties, selenate is described to be reduced over sulfate reducing pathways, which makes the stimulation of selenium oxyanion conversion possible by activating sulfate reducing bacteria (SRB). On the other hand selenate is described to be a specific inhibitor for SRBs. Consequently, an intensive investigation of the influence of sulfate on selenium conversions was conducted.

Two UASB bioreactors (working volume of 0.46 L) were incubated with anaerobic granular sludge, operated at a superficial upflow velocity of 1 m h-1 and a hydraulic retention time of 6 h. Lactate was used as carbon source at an organic loading rate of 5 g COD L-1 d-1. In order to enrich sulphate reducing consortia, one rector (R1) received sulphate at an COD/Sulphate ratio of 0.5 during period an initial period of 23 days. The second reactor (R2) received only lactate but no sulphate as a control. Due to the high toxicity towards sulphate reducers, inhibitory concentrations for selenate were determined previously and influent concentrations chosen accordingly for period 2 (days 24 to 35). During this period, only the sulphate free reactor removed considerable amounts of selenate. This could be explained by the high ratio of sulphate to selenate and concurrence for the active enzymes. Therefore, the sulphate concentration was lowered for period the subsequent period (36 days onwards) while the selenate load was kept constant, as the IC50 values were comparable regarding the inocculum. Immediately after changing the sulphate load, R1 showed high selenate reduction (83-90%) while in R2 the selenate removal rate decreased over the time (from 54 to 37%). This underlines clearly the important role of sulphate reducing bacteria during the reduction of selenium oxyanions.

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Chelate-assisted phytoextraction of Cu and Pb with the aid of organic acids: toxicity, enhanced uptake and biodegradation

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Heavy metal contamination in soils results in their accumulation thus leaving these soils unavailable for agricultural use. Therefore, a need exists for cost effective remediation procedures. Phytoextraction, the use of plants to extract contaminants from soils and groundwater to the aboveground parts of the plant via the roots, has revealed great potential, but is limited by the fact that plants need time and nutrient supply and have a limited metal uptake capacity. EDTA and further synthetic chelators have shown positive effects in enhancing heavy metal extraction through phytoremediation, but have also revealed negative side effects such as high phytotoxicity and leaching of essential metals. Application of organic acids (citric acid, tartaric acid, and oxalic acid) to mobilize heavy metals and to improve the phytoextraction of heavy metals-contaminated soil was investigated. We performed slurry and column experiments with organic acids and EDTA on a silty-loamy sand agricultural soil collected from Melaten field in Aachen, Germany. Tobacco (Nicotiana tabacum) was used as a model plant for phytotoxicity and phytoextraction experiments. We quantified the enhanced uptake of heavy metals in plant tissues by means of microwave digestion and subsequent AAS (atomic absorption spectroscopy). The uptake of copper assisted by organic acids was increased by over 200%. In comparison to EDTA significant differences in their toxicity towards tobacco was visible. The biodegradation of organic acids via oxitop-system (DIN 19737) and its influence on the bioavailability and mobility of heavy metals was observed. The biodegradation increases the pH of the soil significantly and subsequently reduces the mobility and bioavailability of the heavy metals studied. Additionally a characterisation of the microorganisms involved in the biodegradation of the above mentioned organic acids war performed via sequencing. Finally, the feasibility of the use of organic acids for the enhanced phytoextraction of heavy metals in soil is discussed.

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PL7 Interactions between organic acids and siderophores at the oxide-water interface

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Microorganisms and plant roots release a variety of different organic compounds into the soil environment, including carboxylic acids, phenols, surfactants, polysaccharides, and siderophores. The release of organic acids and siderophores is often a specific response to low availability of essential nutrient elements. For example, under Fe-deficiency roots of many grasses release siderophores, which are very strong and specific complexing ligands for Fe(III).

To better understand the surface chemical aspects of siderophore-promoted iron acquisition by plants and microorganisms, we have investigated the interactions between oxalate and siderophores controlling the dissolution kinetics of goethite (α -FeOOH), an important iron oxide mineral in soils. A bacterial siderophore, desferrioxamine-B (DFO-B), and purified phytosiderophores collected from Fedeficient barley plants were used in the experiments. Dissolution of goethite was studied in batch experiments at constant pH (6 or 8) by monitoring the total dissolved Fe concentration in solution as a function of time. Dissolution rates were calculated from the slope of the linear increase in dissolved Fe, excluding possible fast initial dissolution reactions. The dissolution of goethite was studied in the presence of constant total concentrations of oxalate and siderophores, and under constant oxalate concentration with step-wise increased siderophore concentrations, respectively.

Strong synergistic effects were observed between oxalate and siderophores in ligand-controlled dissolution of goethite, meaning that the dissolution rates were much higher in the presence of both oxalate and siderophore ligands than expected from the sum of rates of oxalate- or siderophore-promoted dissolution alone. Experiments with step-wise additions of siderophores suggested that oxalate leads to the slow formation of a "labile" iron species on the surface of goethite, which is rapidly released into solution upon increase of free siderophore ligands. The molecular nature of the "labile" Fe still remains unclear, however. This synergistic dissolution mechanism may play an important role in the rhizosphere of plants, which are known to release pulses of siderophores rather than a constant flux.

In a similar dissolution experiment with colloidal UO_2 particles under anoxic conditions, we further demonstrated that the release of dissolved U(IV) was strongly enhanced in the presence of siderophore ligands, which also form stable complexes with U(IV). These results point to the possible role of siderophores in the bioavailability of uranium at sites contaminated with UO_2 .

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Adsorption of freons by calcium carbonate under atmospheric conditions

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In the atmospheric layer nearest to the Earth's surface (troposphere) various processes occur, which yield a decrease in the concentrations of gaseous atmospheric pollutants. The main process in the mixing by air flows that causes the dilution of a pollutant. The process leading to cleaning of the ambient air include also gas-phase (homogeneous) chemical reactions of pollutant oxidation by strong oxidants, for example, ozone or atomic oxygen formed from ozone under the solar irradiation.

Heterogeneous processes involve the adsorption of gas molecules by the Earth's surface, vegetation, inner and outer of buildings and constructions, as well as the absorption of molecules by water of rivers, lakes, seas, and oceans. Heterogeneous processes (interfaces: gas - liquid aerosol, gas – solid aerosol) can also result in removal of pollutants from the gas phase of atmosphere. For example, such processes clean the air during rains (absorption process), snowfall, and dust storms (adsorption process).

Adsorption on the surface of aerosol particles occurs due to their permanent residence in the troposphere till the establishment of the adsorption (absorption) equilibrium, determined by the concentration of a pollutant in the gas phase and the adsorbability of solid aerosol particles or their solubility in the liquid aerosol.

It is known from the experimental data that the elemental composition of solid aerosol particles in the troposphere is qualitatively (and even quantitatively for many elements) close to that of the lithosphere. Chemical compounds comprising the tropospheric solid aerosol include calcium carbonate (minerals of the carbonate class: calcite and aragonite). For example, in the solid aerosol collected from the ambient air onto a filter, the content of calcium carbonate achieves 10 weight percent of the total amount.

We have investigated the dark and light-induced adsorption of Freons 12 (CF_2Cl_2), 22 (CHF_2Cl), and 134a (CF_3CH_2F) on samples of calcium carbonate prepared using different methods. For comparison, some results obtained for samples of magnesium oxide, having high photosorption activity for Freons, are presented as well.

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Colloidal mesostructures induced by interfacial non-homogeneities at the airwater interface

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We study the formation of colloidal mesostructures induced by interfacial nonhomogeneities at the air-water interface. The inhomogeneous interface is due to the presence of two liquids with different surface tensions. The effective potential between pairs of interacting particles is assumed to be composed by two terms only, the first is due to the dipolar force (repulsive) between the partly immersed parts of charged microspheres and the second is connected to the interfacial stress caused by the difference in surface tension of both liquids. An interaction potential as simple as this is able to reproduce the experimental mesostructures of colloids confined at the air-water interface found by different authors. As a consequence, the mechanism behind the phenomenon of longrange attraction between colloidal particles that are confined at the air-water interface and form mesostructures is not associated to any non-accepted physical interaction but to the formation of an inhomogeneous interface due to the presence in that interface of two liquids with different surface tension.

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Influence of synthetic and biogenic surfactants on ligand-promoted dissolution of iron and aluminum oxides

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Bio-surfactants are released by a range of microorganisms and plant roots in soils and sediments. They have a strong affinity for solid-liquid interfaces and change their physico-chemical properties. These effects play an important role in biofilm formation and nutrient acquisition by organisms.

We investigated the influence of adsorbed synthetic (Sodium Dodecyl Sulfate, SDS) and biogenic (mixture of two Rhamnolipids, Rhl 1 and Rhl 2) surfactants on the surface properties and ligand-promoted dissolution of goethite (α -FeOOH) and boehmite (γ -AlOOH) in the presence of siderophores and other ligands. Siderophores are low molecular weight biogenic ligands with a very high affinity and specificity for iron. We used the siderophores desferrioxamine-B (DFOB) and desferrioxamine-D (DFOD). The ligands were selected according to their contrasting characteristics in terms of charge and hydrophobicity. We observed by measuring the electrophoretic mobility that the adsorption of both surfactants reversed the surface charge of goethite from positive to negative at pH 6. The adsorption of the siderophores DFOB and DFOD increased similarly with an increasing SDS concentration despite their difference in charge (DFOB is positively charged, DFOD is uncharged at the experimental pH). This suggests that the hydrophobic forces involved in the adsorption of the siderophores are more important than the electrostatic interactions in presence of surfactants.

Dissolution rates of goethite and boehmite increased with surfactant concentrations. This effect was more pronounced at low surfactant concentrations. However, the relationship between adsorbed ligands and dissolution rates was not linear as predicted by the rate law of ligand controlled dissolution.

The results demonstrate that adsorption of surfactants on mineral surfaces has a significant influence on surface properties and surface controlled processes such as biological nutrient acquisition, weathering, and adsorption of organic compounds.

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ABSTRACTS (Posters)

P1

Role of organic matter on the mobility of radiocesium in agricultural soil

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Cesium-137 is an important radionuclide because of its long radiological half-life (30 y) and high fission yield from 235U and 239Pu. In a natural soil environment, the presence of 137Cs is due to releases from nuclear weapons testing and nuclear accidents. In order to reduce radiation dose from 137Cs, it is important to know its mobility in soil. Although 137Cs is immobilized in soil surface layer, there is a small 137Cs fraction which moves faster towards deeper layers. Soil organic matter (SOM) might affect this phenomenon because SOM is a reactive colloid, but this has not been clarified yet. Therefore, tracer studies were carried out to clarify the effect of SOM on Cs mobility in soil.

Soil-soil solution distribution coefficients (Kds) of 137Cs were measured for 87 Japanese agricultural soils by a batch method to evaluate the adsorbability of 137Cs onto soil. The soil samples contaminated with the 137Cs tracer were saved for further study. For 16 soil samples, the SOM-bounded 137Cs percentage was determined by an extraction with 0.1 M Na4P2O7. Then reversibility of Cs sorption on SOM was evaluated especially for the soil humic acid (HA) fraction. The HA fraction was separated by adding H2SO4 to the Na4P2O7 solution to reduce pH to 1.5, then the HA-137Cs was left in contact with 1 M ammonium acetate (NH4OAc) to extract exchangeable 137Cs from HA by adjusting pH with H2SO4. In order to determine the effect of dissolved organic matter (DOM) on Cs chemical forms in soil solutions, the amount of 137Cs bound to DOM was determined for 30 soil samples by adding HCl to the soil solution to separate the HA-bounded 137Cs fraction as precipitate.

The observed Kd values ranged from 215 to 43400 (L/kg) with a geometric mean of 2210 L/kg. This high Kd values indicated that only 0.02-4.45% of the added 137Cs was distributed in the soil solutions. For the soil samples, Kds positively correlated with soil clay contents, while a negative correlation was found with carbon contents. These results suggested that one of the major 137Cs adsorbents in soil was clay minerals; however, 137Cs adsorption on the soils was inhibited by SOM. Among soil types, relatively low Kd values were observed for Andosols. The high SOM contents of Andosols would possibly affect Cs mobility.

Results of the selective extraction with Na4P2O7 showed that 3-17% of soil-adsorbed 137Cs was in an SOM-bounded form. Among the SOM-bounded Cs, HA-Cs was studied further. It was observed that 27-100% (average: 63%) of HA-bound Cs was exchangeable with NH4OAc.

The effect of DOM in soil solution was also verified. About 5-82% (average: 45%) of 137Cs in soil solution was HA-bound form for 25 soil samples. However, no DOM-bounded 137Cs was observed for 5 soil samples, possibly due to low solubility of their SOM. These results suggested that a part of the added 137Cs was distributed in soil solution as DOM-bound form in many soils, although most of the added137Cs was fixed on the soils. Possibly, SOM could increase the mobility of accidentally released 137Cs by inhibiting Cs adsorption in soil and by binding Cs as exchangeable and DOM-bound forms.

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P2

Water repellency, kinetics and nature of wetting in urban soil samples

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Although the wettability is an important factor for sorption and transport processes in soils, the knowledge about the reasons for water repellency and its effects on other soil properties is still insufficient. Wetting kinetics are strongly related with the mechanism of wetting and thus may serve as means to investigate the origin of soil water repellency. Wetting kinetics of soils have however been scarcely investigated yet. Todoruk et al., 2003 and Schaumann et al., 2005 applied 1H-NMR Relaxometry to monitor wetting and swelling kinetics of soil samples. Schaumann et al., 2005 found time constants of water redistribution of 5-10 days in a soil sample with a WDPT of 10 hours. This emphasizes that even in regions with only weak water repellency, water redistribution due to rewetting may still be slow, and is expected to affect water flow as well as the environmental availability of enclosed pollutants.

For further understanding of these apparent differences, it is necessary to separate the process of infiltration from the development of the surface properties initiated bv the interaction between soil and water. We investigated pairs of water repellent and wettable soil samples from the location of the interurban research group (Berlin, Tiergarten and Berlin-Buch) in terms of drying and remoistening characteristics. We monitored the change of sessile drop shape on soil samples in the course of soil-water contact time for two urban soils at three different temperatures. From the time dependence of the sessile drop contact angle, rate laws and rate constants of wetting were derived. The kinetic parameters differ strongly between both investigated locations and even indicate different types of rate controlling mechanisms (Diehl and Schaumann, 2006). The differences are underlined by additional differences in the development of water repellency upon drying, storage and remoistening asdifferences in some physicochemical soil characteristics. as well These results show the relevance of kinetic investigations to assess soil water repellency, and they clearly indicate that the origin of soil water repellency is strongly determined by individual locational conditions.

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$\mathbf{P3}$

Influence of soil characteristics and evaporation processes on the raising up of salt and pollutants in Mediterranean mining areas

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Some mining areas are plenty of pollutants, such as heavy metals, but also have a lot of salts that can rise up by capillarity processes, dragging with them high amounts of metals. This fact can be of big importance regarding the health of the ecosystems and populations placed around these mining areas. Depending on several soil characteristics such us porosity, medium pore size, water content, pH, soil salinity and thermodynamic surface properties, but also by the effect of evaporation processes influenced by average air temperature and air saturation status, there are important raising up processes of salt and associated pollutants under Mediterranean climate mining areas. This study has been focused, mainly, on the study of the rising up phenomenon of the salts and dragged heavy metals, depending on soils characteristics and weather conditions. In this sense, higher amounts of salts rise up in salty soils, with a medium-small porous size and under dry weather conditions. Otherwise, soil pH seems to have a great influence on metal enrichment of these salts that can appear on soils surface.

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$\mathbf{P4}$

Characterization of soil and sediments from a Mediterranean mining area and its relationships with metal mobility

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Mobility of heavy metals in soils, waters and sediments have received attention in last years. In a solid matrix, such as soil and sediment, metal mobility and leaching depends on many physicochemical properties of those, such as chemical form, reactions, solubility, density, porosity, pH, electrical conductivity, water content, electrokinetic, surface thermodynamic... All these properties of the materials involved can be affecting to the metal mobility and leaching. Regarding this, the research has been focused, first, on the study of the soluble metal concentration, pH, electrical conductivity (EC), and water content variation depending on samples depth of different soils and sediment layers in a drill taken in a wades riverbed placed in a Mediterranean mining area. Results show high soluble Al, Pb, Zn and Fe concentration (tens of ppm). The relationship between pH and depth shows a variation between 2.5 and 6.7, with a minimum placed between 1 and 2 m. On the other hand, EC has a maximum around 4 mS/cm between 1 and 4 m, and a minimum around 3 mS/cm between 0.3 and 3 m. The water content is higher in the interval 2-3 m depth with values around 25 % w/w. All these results show the high sensitivity of the systems to the electrokinetic and surface properties of the involved soil and sediments due to the solid/liquid interfaces of the systems. Since present colloidal particles in the can carry adsorbed metals, the work is being completed with a determination of the electrokinetic and surface thermodynamic properties of the samples. This kind of study can provide information on the mobility and dynamics of metals in polluted soils and sediments.

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P5

Alkylpyridinium chloride surfactant binding to humic and fluvic acids

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Surfactants are used in many personal care, household and industrial applications. Part of these surfactants is discharged and may come into contact with natural waters and soils. The interaction between surfactants and mineral oxides is well understood (mainly for industrial applications), but the interactions of surfactants and humic substances are not well studied. Humic and fulvic acids are the commonly observed humics in aqueous environment and they play an important roll in the distribution of contaminants. In this research, we have investigated cationic surfactant binding to several humic acids (HAs) and fulvic acids (FAs).

Aldrich humic acid (AHA), Dando humic acid (DHA), Inogashira humic acid (IHA), Laurentian fulvic acid (LFA), and Strichen Bs fulvic acid (SFA) were used. The surfactants, n-dodecylpyridinium chloride (DPC) and n-hexadecyl- or cetyl-pyridinium chloride (CPC) were supplied by Aldrich and used as received.

Monomer surfactant concentrations were measured with cationic surfactant selective membrane electrodes. A home-made Ag/AgCl electrode was used as inner electrode. Surfactant concentrations in the reference solution of the membrane electrode were 2.5x10-4 M for DPC and 2.5x10-5 M for CPC. As reference electrode a commercial Ag/AgCl electrode was used.

Binding isotherms of DPC to the HAs and the FAs and that of CPC to AHA were obtained from surfactant titrations in the presence of the HAs and FAs at an electrolyte concentration of 0.005 M NaCl and an initial pH 5.2j0.1. The concentration of the HAs and FAs was 0.1g/L. 0.25 g AHA/L was applied for the CPC-AHA system. Bound amounts of surfactant (mol/kg) were calculated from the added amount of surfactant, the measured equilibrium surfactant concentration and the total solution volume. pH changes during the binding experiment were measured and the H+ release from the HAs and the FAs was calculated. The iso-electric point of the DPC-AHA complex was measured with the Particle Charge Detector PCD 03 pH (MÜTEK).

The following results were obtained from the binding experiments. 1. The bound amount at low DPC concentrations (<10-4M) is in the order AHA >> IHA > DHA >> LFA = SFA.

2. Based on log-log plots of the adsorption isotherms no cooperative binding is detected for CPC-AHA, DPC-HA and DPC-FA systems. Near "Henry-behaviour" is observed at the initial binding stage.

3. The CPC-AHA binding is stronger than the DPC-AHA binding due to the longer C chain of CPC.

4. The charge of the DPC-AHA complex changes from negative to positive at a bound amount of about 2 mol/kg. This adsorption corresponds to the point where the surfactant ions completely neutralize the AHA articles.

5. H+ release is relatively small and starts after charge compensation.

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$\mathbf{P6}$

Direct movie analysis of Brownian motion of colloidal particle and its application to diffusion constants of small flocs

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Analysis of movie record of Brownian motion of single colloidal particle under microscope was conducted to determine the Stokes diameter via diffusion constant. Mean square displacements of single particle for certain time interval were obtained from the trace of Brownian motion recorded in the computer. Appropriate conditions of this method were examined varying particle size, shutter interval, the number of frames, magnification. An additional test using ultramicroscopy was also carried out. As a result, determination of Stokes radius with relative error of less than 10% was achieved with processing 1000 frames. The value is slightly higher than 6% which is statistically predicted. The difference between true centre of mass and obtained centre of mass via thresholding process can be considered for the reason of increment of the error. Applicability of the developed method was tested to determine the Stokes diameter of coagulated flocs formed of uniform latex particles. The obtained diameter of doublet was consisted with the values determined by disc-centrifuge method [1] and other experiment [2]. It was also confirmed that Stokes radii of flocs composed of primary particles up to ten obey power law, and its fractal dimension was corresponded to 2.5 for cluster-like flocs.

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$\mathbf{P7}$

Deposition and subsequent release of Na-kaolinite particles by adjusting pH in the column packed with standard Toyoura sand

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Release of colloids in soil is related to their depositing process. In the present study, release behavior of kaolinite particles by means of pH adjustment from the column packed with standard Toyoura sand was analyzed after the deposition experiment under controlled conditions.

Commercially available kaolinite particles were saturated by NaCl. Suspension of the kaolinite under the condition of pH4.7 and ionic strength of $1*10^{(-4)}M$ were used for depositing material. With this solution condition, measured zeta potential of kaolinite and Toyoura sand were -25mV and -20mV, respectively. Different volume fraction suspensions were pumped into the column. The deposition experiments were carried out for five hours. Then, the influent was switched to $1*10^{(-4)}M$ NaOH solution to induce release of kaolinite by chemical perturbation. Turbidity of effluent was measured by absorption spectrophotometer. Kaolinite particles in effluent were observed through microscope, simultaneously.

The result showed that the peak of breakthrough curve appears more slowly with an increase of volume fraction of kaolinite in the influent. Before the peak, most of kaolinite particles were detected as individual particles, however, after the peak, kaolinite particles are detected more frequently as flocs.

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P8 Restructuring of Small Flocs Formed with Polyelectrolytes

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The morphology of small flocs, formed of negatively charged polystyrene latex (PSL) particles with cationic polyelectrolytes of different molecular weights, were investigated to clarify the restructuring process of flocs. Experiments were designed in order to elucidate the effect of adsorption kinetics of polyelectrolytes on the restructuring process of flocs. In the experiment, flocs were formed in the standard mixing apparatus and were picked up into capillary cell for monitoring through microscope. The relation between the maximum distance in the projection of formed flocs and the number of primary particles composing the floc was used as an index of the floc structure. It was found that restructuring occurs facilely under the condition of high ionic strength. However, in the solution of low ionic strength, the degree of restructuring varies with molecular weight. Flocs with most bulky structure were detected when the highest molecular weight of polyelectrolyte was applied. Such difference of the floc structure corresponds to the results of the reconformation process of adsorbed polyelectrolyte on the PSL surface, studied by electrophoretic mobility reported previously [1].

[1] K.Aoki and Y.Adachi, Submitted.

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$\mathbf{P9}$

Sorption/desorption properties of heavy metals on montmorillonite with special reference to charge characteristics

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Sorption and desorption properties of cadmium and copper on montmorillonite were determined as the function of pH and electrolyte concentration. The basal surface of montmorillonite carries a constant negative charge which is attributed to the isomorphous substitution, whereas the charge of edge surface depends on pH and shows an amphoteric character. In the low pH regions, adsorbed Cd was easily desorbed by subsequent Ca(NO3)2 extraction. In the pH regions above the reported PZC value (ca. 6.5) for the montmorillonite edge, adsorbed Cd was hardly desorbed by subsequent Ca(NO3)2 extraction but quantitatively desorbed with HCl. The amount of adsorbed Cd corresponded with the CEC value throughout the tested pH, whereas more Cu than CEC was sorbed especially in the high pH regions. For the purpose of increasing the edge surface, montmorillonite was milled manually in the agate mortar for 10 minutes. Although the XRD patterns of montmorillonite before and after milling were identical, significant decrease in the particle size distribution was observed after milling. The milled montmorillonite not only enhanced Cd sorption but also decreased Cd desorption, probably due to adsorption of Cd on the newly created edge surface.

Although the edge surface of montmorillonite accounts for minor parts of total surface area (ca. 1%), remarkable contribution to physical behavior such as dispersion/ flocculation, viscosity, and thixotropy has been reported, which is attributable to the presence of amphoteric, variable charge on the edge of montmorillonite. Our results strongly indicate that distinction of relevant charge type is also important in heavy metal sorption/desorption on montmorillonite.

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Enhancement of herbicide photodegradation in the presence of cyclodextrins and different soil colloidal components

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The photochemical behaviour of the herbicide norflurazon in the presence of different colloidal components of the soil and several cyclodextrins (CDs) has been investigated. The selected colloidal components were: a natural metal-fulvic acid complex, two synthetic humic acids, three different standard clay minerals (illite, kaolinite and montmorillonite), a synthetic acicular goethite, and natural clay fractions extracted from two different soils. The CDs employed were: beta-cyclodextrin (BCD), hydroxi-propyl-beta-cyclodextrin (HPBCD) and methyl-beta-cyclodextrin (RAMEB).

The interaction of norflurazon with BCD, HPBCD and RAMEB yielded the formation of inclusion complexes at a 1:1 stoichiometric ratio in solution. Apparent stability constants of 360.16, 359.47, and 558.51 M^{-1} and an increase in herbicide solubility by up to 5-, 35- and 54-fold for BCD, HPBCD and RAMEB, respectively, were obtained from the phase solubility diagrams at 25 °C in water.

In general, the presence of the different soil colloidal components in aqueous suspension provoked the reduction of norflurazon photodegradation rate, which followed a first-order kinetic. In contrast, the presence in such systems of the different CDs selected showed an inductive photodegradation effect on the herbicide, which could be mainly assigned to the inclusion effects of CDs to catalyze interactions between norflurazon and certain reactive radicals generated by the different colloidal components. In conclusion, this work reveals that the effect of the CDs on the herbicide enhanced solubilization coupled to an increased photodegradation could be a promising method for pesticidecontaminated soil remediation.

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Ethylcellulose microspheres for reducing movement of alachlor in soil

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For a soil applied herbicide to be effective in controlling susceptible weeds, the available active ingredient must be above a minimum threshold concentration in the soil matrix for a given period of time. However, application rates for conventional herbicide formulations are generally greater than the minimum threshold concentration, in order to overcome losses from degradation, leaching, volatilisation, and sorption during the time needed for weed control. Because of the excess of active ingredient initially applied, water leaching through the soil just immediately application creates an increased potential for herbicide leaching, with the consequent possibility of groundwater contamination.

Alachlor is a preemergence herbicide for selective weed control in various field crops. It suffers rapid loss of biological activity due to leaching down to deep layers in the soil profile. Although some extent of leaching is necessary to achieve proper weed control, there are three problems associated with herbicides leaching: (1)Leaching to the root zone of sensitive nontarget crops results in crop injury; (2)leaching below the root zone of the target weeds may reduce the herbicidal activity; and (3)leaching may result in groundwater pollution.

In order to diminish alachlor problems of leaching in sandy soils, avoiding its groundwater contamination, we describe the preparation, physicochemical characterisation and application to soil of ethylcellulose microspheres containing the herbicide alachlor.

Microspheres were prepared by the oil-in-water emulsion solvent evaporation technique, using chloroform as internal phase. Ethylcellulose of different densities (EC40, EC10), were used. To obtain the microspheres, certain parameters (pesticide / polymer ratio, the percentage of emulsifying agent, shaking velocity, addition of pore forming agent) have been changed. Physicochemical characteristics of the microspheres obtained were studied by different techniques. Their size distribution was determined, their surface morphology was studied by scanning electron microscopy (SEM) and several parameters such as rent of production, encapsulation efficiency and pesticide loading in the microspheres, have been also calculated.

In vitro release studies of norflurazon and alachlor in water from the different microspheres obtained were performed. The dissolution profiles of commercial norflurazon and microspheres formulations have been compared. In all cases the release of norflurazon from microspheres was retarded when compared with that of commercial herbicide. The percentage of the herbicide release was related to the properties of the different microspheres obtained, such as particle size distribution, herbicide loading and surface morphology, depending on the percentages of emulsifying and pore-forming agent used. An empirical equation was used to fit the herbicide release data, indicating that the release of norflurazon from the various formulations is controlled by a diffusion mechanism.

The transport of alachlor through soil columns was also tested in order to know the depth reached by the herbicide depending on the formulation used. The availability of norflurazon in a soil-water system was greatly diminished, reducing their losses due to leaching, and the amount of herbicide remaining distributed among the different depths in the soil column was higher in the upper ring and gradually lower amounts in the deeper ones.

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Effect of charged polyelectrolytes on the electrophoretic behavior, stability, and viscoelastic properties of montmorillonite suspensions

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The stability and rheological properties of clay minerals strongly depend on the interfacial properties of the clay/solution interface. These properties can be modified by the adsorption the different electrolytes in solution and, in particular, the adsorption of organic polyelectrolytes can provoke a wide variety of behaviors depending on the charge, molecular weight, and concentration of the polymer molecules.

This work is devoted to the study of the rheological (viscous and viscoelastic) properties of sodium montmorillonite suspensions in aqueous media containing polyelectrolytes in solution. Two different polyelectrolytes are employed: polyacrylic acid (PAA) and polyethyleneimine (PEI). PAA can bear negative charge, thus acting as a polyanion, while PEI can be considered as a polycation, although the bulk charge of both polymers is strongly dependent on pH of the solution.

The rheological behavior of clay suspensions is essentially determined by the electrical state of the faces and edges of the laminar clay particles. In order to analyze the changes in the interfacial electric potential of clay surfaces, the zeta potentials of both faces and edges were estimated from electrophoresis measurements for different solution compositions. The yield stress and the storage modulus of suspensions were determined demonstrating that only in some particular conditions the storage modulus is correlated with the changes in the face-to-face, face-to-edge, and edge-to-edge electrostatic interactions. To explain the observed viscoelasticity of the clay/polyelectrolyte suspensions, sedimentation experiments were also carried out in order to detect the changes induced in the stability of the suspensions by polymer addition. Different mechanisms are proposed to explain the wide variety of flocculation/restabilization and rheological phenomena observed.

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$\begin{array}{c} \mbox{Migration modelling of humic acids associated with $Np(V)$ ions considering interaction kinetics and impact of colloids on safety assessment of high-level radioactive waste disposal \end{tabular}$

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Groundwater colloids associating with actinides can act as a carrier for actinides in geosphere and biosphere. Therefore, the safety assessment of high-level radioactive waste disposal is markedly dependent on actinide colloids formation and their migration. In order to improve the reliability of safety assessment, it is important to model the adsorption/desorption among actinide ions, groundwater colloids and surface of the geologic media.

A lot of colloid formation and migration models have been developed. In those models, the data obtained by batch sorption experiments independently were incorporated as a simple sorption isotherm, for example. However, it is well known that the adsorption/desorption of colloids can not be described by simple sorption isotherms. Furthermore, the importance of kinetics of adsorption/desorption interactions has recently been pointed out, especially when the groundwater flow rate is relatively high.

In the present work, the migration model of colloids associated with actinides was developed, considering the advection/dispersion of colloids and ions, the sorption equilibrium and kinetics among ions, colloids and solids phases, the matrix diffusion of ions and the filtration of colloids. The model was applied to the breakthrough curves of humic acids associated with Np(V) ions through the silicate packed columns. Furthermore, using the model, the impact of colloid formation and migration on safety assessment of high-level radioactive waste disposal was evaluated.

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Experimental and theoretical study of montmorillonite-glyphosate surface complexes

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Glyphosate (N-phosphonomethylglycine), one of the most employed herbicides around the world, interacts strongly with many soil components. It forms strong complexes with many metals in solution, and it is adsorbed through inner-sphere complexation to ironand aluminum oxides. The chemical group responsible for the adsorption processes is the phosphonic acid moiety. This phosphonic acid group through its very stable C-P bond makes glyphosate extremely resistant to chemical hydrolysis, thermal decomposition and photolysis

Herbicides are generally adsorbed onto the soil components such as clay minerals, organic matter, metallic oxides and humic substances. In particular, expansive clays have important implications for agricultural, engineering and environmental purposes. Being montmorillonite the most common expansive clay found in soils. Montmorillonites have shown a great capacity of adsorption of both metallic cations and organic substances due to their small particle size (<2 μ m), high surface area and isomorphic substitutions in their structure and because there have at least two types of sites available for adsorption process.

Glyphosate adsorption isotherms were measured by ICP or CI. Surface coverage was calculated by the difference between initial concentration and the concentration remained after 24 hs equilibrium. The adsorption dependence with pH was also measured and the thermodynamic adsorption parameters were calculated. The adsorption isotherm showed a multisite shape. XRD and XPS were made on samples with glyphosate concentration correspondent to the different sections of isotherm and they were compare with those made without adsorbed glyphosate XRD and XPS were also carried out at different pH values due to the influence of the pH on the montmorillonite structures and glyphosate molecule. The influence of the glyphosate content in the interlayer, was pointed out by a d(001) reflection parameter shift while XPS results indicated that the ratio of [NH]/[NH2+] increase as the amino group of surface complexes is deprotonated.

The interactions of glyphosate molecules with montmorillonite were studied with theoretical methods ranging from ab initio to molecular mechanics calculations to explore the ways in which the molecule may bind to the interlayer surfaces of the mineral.

To model the interaction of the fully protonated glyphosate molecule with montmorillonite, molecular modeling calculations were performed with the glyphosate molecule placed in the montmorillonite interlayer and allowed to move freely, without constraints.

The structures of the surface complexes are proposed based on the XPS spectra, XRD, and theoretical molecular modeling techniques. The role of the carboxylic acid and amino group in the structures of the surface complexes of the herbicide with montmorillonite is also discussed.

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P15 The Adsorption Properties of Al-Pillared Bentonites

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The alumina -pillared clavs used mainly as catalyst in a number of catalytic reactions have high porous and stable structures. Due to these properties, it is possible to use the pillared clavs (PILC s) as adsorbents. Especially their stable structures will form an advantage in the regeneration of adsorbent. In this work, the adsorption properties of PILC s were investigated by using phenol as model pollutant. The alumina-pillared bentonites were prepared by the conventional method of pillaring involving the mixing a dilute clay suspension with a dilute pillaring solution. To study the influence of exchangable cations on textural properties of the PILCs, the OH/Al3+ and Al/Clay ratios were changed. During the synthesis, Al/Clay ratio was kept constant as 1.8 and/or 2.5, while OH/Al3+ ratios were changed as 1.44, 2.0, and 2.5 for each trial. The XRD analyses show that the basal spacing is increased by 3.5 Å, 6.22 Å, and 5.79 Å for the adsorbents synthesized by 1.44, 2.0, and 2.5 OH/Al3+ and 1.8 Al/Clay ratios, respectively. For the adsorbent prepared by using 1.44 OH/Al3+ and 2.5 Al/Clay ratios, this increase is 5.72 Å. The adsorption experiments were planned in two groups: kinetics and isotherm experiments. The batch technique was used in the experiments. The kinetic studies revals that the equilibrium is established approximately in 150 minutes. A series of isotherm experiments were also conducted by HDTMA-bentonite to compare the adsorption behavior of PILC s. The results of preliminary experiments reveals that the adsorbed amounts are higher in the case of PILC s. However, the adsorbed amounts remain nearly constant when the OH/Al3+ ratio is increased from 1.44 to 2.0 at 1.8 Al/Clay ratio although a considerable increase in basal spacing is obtained.

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Role of mineral dissolution of a natural sand in the tributyltin behaviour at very low concentrations

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To forecast the change of water quality, it is necessary to study the fate of contaminants in aquatic systems. It is controlled by the interactions between the different species of contaminants and the compartments of aquatic systems. The present work focused on the behaviour of an organotin, the tributyltin noted TBT, during its migration through different porous media. TBT, the sources of which are very diverse, is a very toxic chemical even at very low concentration. TBT plays the role of an endocrinal disrupter with a long life-time in the environment.

Experiments were carried out with flow-through reactors at low concentration in the presence of an aquifer material, a natural quartz sand (99 % of quartz, and traces of Fe and Al (hydr)oxides or clays). Mean pore velocity, chemical composition of water, pH were chosen in order to mimic the fate of such a micropollutant in natural aquatic system. Sorption experiments were performed by injecting TBT concentration from 0 to 1 nM, followed by several steps until 1 \cdot M. TBT were analysed by GC-PFPD (detection limit below 1 ng/L), and the other elements by ICP-AES.

The main goal of our study was to identify main mechanisms such as sorption and to quantify physico-chemical parameters, which control the behaviour of TBT. Moreover, we paid attention to the potential role of minerals which are present at the surface of the natural quartz sand.

We showed that TBT sorption behaviour is non-linear even at trace level and constant pH. On the other hand, depending strongly on pH (2, 4 and 6), Al, Fe, Si and S are present, mainly due to the mineral dissolution. At constant pH, we observed that an increase in the TBT concentration induces an increase in the Fe concentration. This could be due to the competition of TBT and Fe for the same silica surface sites. This is consistent with previous results where we have shown that TBT has a stronger affinity for pure amorphous silica or quartz than for clays or Fe or Al hydroxide minerals. The source of S, the concentration of which is more or less constant with pH, is mainly due to the redox dissolution of pyrite, which is present at very low level in this sand. For Fe, concentration increased with decreasing pH where dissolution of both pyrite and hydroxide is facilitated. In this presentation, we will show why it is important to work at very low level and to know more on the trace minerals in order to understand their effect of on the TBT breakthrough through sediments for environmental conditions.

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Retention of pesticides onto vineyard soils and a lignocellulosic substrate. Contribution to the improvement of the water quality

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This study is part of the AQUAL project, which is a multi-field research program that aims at improving the quality of the water in the basin of the river Vesle (a river that runs across the Champagne area). This better quality of the water will be reached by controlling the diffuse pollution in the rural areas of this basin, namely the large-scale farming fields and vineyard zones around the city of Reims. Our contribution to this program is twofold: on the one hand, the understanding of the processes involved in the transfer of the contaminants towards the aquifers, and, on the other hand, their reduction by using an adsorbing biomaterial, i.e. the lignocellulosic substrate (LS) extracted from wheat bran.

We specifically studied the retention of the terbumeton and its main metabolite, the terbumeton desethyl, on five soil samples representative of the Vesle basin: two samples from a bare vineyard soil (one taken from the top of a parcel and one from the bottom), one from an undergrass vineyard soil, one from an underbark vineyard soil and a last one from a soil of a large-scale farming field. The influence of copper, an ubiquist metal cation, onto the pesticide sorption was also studied.

After the determination of the structural and physicochemical characteristics of the soil samples (granulometry, mass composition, density of sites, etc), the binary systems pesticide/soil, pesticide/metal and soil/metal were studied. The adsorption curves as function of the pH and the adsorption isotherms as function of the concentration show that the terbumeton is significantly adsorbed onto the bare and under-bark soils. The retention of the pesticides by soils is independent of the pH except for the under-bark vineyard soil. On the other hand, the under-grass and large-scale farming field soil samples adsorbed neither the terbumeton nor the terbumeton desethyl. The desorption kinetic study indicates that the pesticides are desorbed very slowly and in a small quantity. These differences in affinity towards pesticides are partly explained by the composition of the soil samples. Indeed, the two soil samples that do not retain the pesticides are those who are very rich in limestone (70 %).

The study of the adsorption of the terbumeton and the terbumeton desethyl was also carried out with the lignocellulosic substrate (LS), a biomaterial that proved to be rather effective in the remediation of pollution. Indeed, the LS can be used in the retaining tanks that collect the surface waters of the vineyard parcels, in the purification stations for the depollution of water, in co-operatives or at the farmer s or vine grower\ s place for the cleaning of the tanks and the treatment machines. The use of LS is patent pending.

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Characterization of non-colored river water humic substances

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In natural water systems, organic matter, humic substances (HSs) in particular, play important roles in mobilization and transport of trace metals throuh complexation. Because of the importance of iron from land to coastal area as a limiting trace-nutrient for primary production, the quantity and quality of HSs in natural water systems have drawn special attention. In this work, HSs in non-colored river water have been collected and purified, and their structural characteristics have been investigated.

Chikugo River. a representative fresh water environment. is located in Kyushu island Japan. HSs in the river water from upper stream to near river mouth were collected by an automatic concentration system, which includes a large column of 900 cm2 cross section filled with 10kg DAX-8 resin. Firstly, the river water was successively filtered through 10mm, 1.0mm, and 0.45mm cartridge filtration membranes. Then, the water was injected into the DAX-8 resin column, after adding a hydrochloric acid solution with a diaphragm pump to keep the pH less than 2. About 10 tons of river waters from 6 sampling points were collected in November, 2005.

The crude HSs adsorbed onto the DAX-8 resin was then extracted by a 0.1mol dm-3 sodium hydroxide solution. The pH of the solution was lowered to 1.2 by adding a hydrochloric acid solution, and the precipitation (mainly composed of humic acid:HA) and supernatant solution (mainly composed of fulvic acid:FA) were separated by centrifuge (2200G x 20min) followed by filtration after storing one night. The HA sample was separated from 0.1 mol dm-3 sodium hydroxide by centrifuge (10,000G x 90min) to remove clay mineral, and treated with 0.15 mol dm-3 hydrofluoric acid +0.05 mol dm-3chydrochloric acid mixture solution. The HA sample was dailyzed (8,000 cut off) against a 0.1mol dm-3 HCl solution until the conductivity of outer solution reached 2mS cm-1. Finally, the sample solution was treated with a protonated cation exchange resincolumn, freeze-dried, and vacuum-heated at 60 Z. Yields of FA and HA from Chikugo river water samples taken from 6 sampling points (Tsuetate, Yuuki, Katanose, Kawashita, Mametsubashi, Tikugo-Ooseki) ranged from 400 mg to 1,100 mg, and from 100 mg to 700 mg, respectively.

The HSs samples were analyzed as follows; elemental analysis (C, H, N, S), functional group analysis (carboxyl, calbonyl, phenolic, and alcoholic hydroxyl groups)by use of 13C-NMR and 1H NMR spectroscopic measurements. Yields of FA and HA from downstream region were always larger than those from upstream region. However, no distinct difference in structural characteristic has been found in FA samples. This may imply that the concentration of FA in Chikugo river may be determined by use of the FA samples as standard materials.

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A Monte Carlo simulation study of the effects of ion size and valence, and polyelectrolyte concentration in mixed size and valence counterion systems of polyelectrolyte solutions

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The electric double layer of a charged polyelectrolyte in the presence of inert salts has been investigated since the pioneering works of Katchalsky and coworkers in the 1950\s decade. Recently, a number of works have been published that apply different theoretical approaches and computer simulations devoted to the calculation of the local surface potential and the distribution of counterions and coions around the polyelectrolyte, aiming to understand its mutual relation.

In this communication we present a Monte Carlo simulation study of the ion distribution in a primitive model of a polyelectrolyte solution containing a mixture of ions with different sizes and valences, assuming either a continuous and uniform distribution of the polyelectrolyte surface charge, or a random distribution of discrete charges fixed on the polyelectrolyte chain. Simple geometries have been considered in both cases. The results are compared with predictions of well-known theories, Non-Linear Poisson Boltzmann (NLPB) and Hypernetted-Chain/Mean Spherical Approximation (HNC/MSA), in order to understand the effects of the ionic size and the ion correlations on the simulation results.

Furthermore, we incorporate the effect of polyelectrolyte concentration by means of a cell model where the van der Waals/Hamaker interactions between polyelectrolytes are neglected. In order to do this, we particularize the simulations for the case of very simple geometries, where only one relevant coordinate is sufficient in order to characterize the average distance between polyelectrolytes.

Finally, we generalize this study to include the case of binding of counterions to charged groups of the polyelectrolyte. In particular, we first consider the protonation of polyelectrolytes and then the competition between protons and divalent cations.

These studies are of great interest in the physicochemical characterization of the complexation of heavy metal ions with natural complexants in aqueous media.

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Surface electrokinetic properties of clays in Okinawa

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The dispersion and runoff of clays in Okinawa Island (Southern part of Japan) depends on the electrokinetic properties of suspended-clay surfaces. To determine surface properties, four kinds of measurements were carried out: (1) surface conductivity measurements as the ratio of the conductivity of the sediment to the conductivity of the supernatant, (2) Electrophoretic mobility measurements using light scattering cell, (3) The acid-base potentiometric titration, (4) Floc diameter measurement by settling velocity. Two kinds of popular clays in Okinawa, Kunigami-maaji (red soil with hematite) and Jaagaru (heavy clay), were selected as the test samples. And for these clays, electrokinetic properties were studied as the function of pH and ionic strength. The results are as followss:

(1) The surface (relative) conductivity of Kunigami-maaji (red soil) increases as the pH increases due to the proton desorption. Red soil showed a rapid increase in the surface charge (or relative conductivity) at pH 6 and higher, corresponding to an abrupt dispersion.

(2) The ζ potential of Kunigami-maaji shows that the particles are negatively charged throughout the almost whole pH range and that the iso-electric point is about pH 2 and abrupt potential change at pH 6. On the other hand, the ζ potential of Jaagaru shows lat curve for pH change like montmorillonite.

(3) The acid-base potentiometric titration shows that Kunigami-maaji resembles kaolinite and Jaagaru montmorillonite.

(4) The increase of ionic strength increases coagulation for Jaagaru suspensions as predicted from the measured ζ potential. But, for Kunigami-maaji, the increase of ionic strength weakens coagulation and slows down the settling velocity.

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Influence of natural organic ligand to U(VI) reduction by Fe(II) in natural underground water environment

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Redox reaction is very important for the migration of actinides in geosphere. Uranium, which is the most important element for the safety assessment, is usually dissolved in solution as U(VI), although the corresponding reduced species, U(IV), precipitates because of the very low solubility. Therefore, reduction of U(VI) to U(IV) greatly contributes to retention of uranium migration in underground water environment. Various metal ions, dissolved organic acids, inorganic or organic colloids coexist in a real environment, and influence redox behavior of the uranium. For instance, it is reported that reduction from U(VI) to U(IV) is facilitated on the surface of the Fe(II) containing iron oxide. It is also reported that the Fe2+ adsorbed polyelectrolyte promotes the reduction of U(VI), as well. However, the influence of dissolved natural organic acids to redox reactions on the solid-liquid interfaces has not been investigated systematically.

In the present study, the reduction behavior of U(VI) in the system of coexistence U(VI), Fe(II), citric acid and various inorganic colloids is investigated for evaluating influence of dissolved natural organic acid and colloids. First, chemical behavior of U(VI)-Fe(II)-citric acid system in absence of inorganic colloids has to be understood beforehand, therefore the redox reaction of U(VI)-Fe(II)-citric acid system was tested. UO2(NO3)2 E6H2O 5mM, FeCl2 5mM, and sodium citrate 1M were mixed under shading, and the absorbance of the sample was measured with ultraviolet-visible spectroscopy (UV-Vis). As a result, increase in the absorbance of U(IV) (fÉ= 665nm) was confirmed with no precipitation in the sample. This indicated that the existence of a citric acid ion promote reduction from U(VI) to U(IV). Further investigation on the reduction of U(VI) in presence of Fe2+, citric acid and several inorganic colloids are performed. The reduction process of U(VI) by Fe(II) on citrate adsorbed solid-water interfaces will be apparent.

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Water solubility enhancement of [60]fullerene in the presence of humic substances

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Water solubility enhancement of [60]fullerene (C60) in the presence of humic substances was investigated by a batch method. In the presence of humic substances, the apparent water solubility of C60 enhanced with increasing the mixing times from 8 to 192 hours. By the mixing for 192 hours, the apparent water solubility of C60 was increased by factors of 10⁹ compared to pure water. The UV-Vis spectra of C60 extracted by toluene from the aqueous of humic substance showed same spectra with that dissolved in toluene, indicating no oxidation of C60. Size fractionation of C60 passed through the filter with 400 nm pore size showed that the 95 - 98 % of C60 could be dispersed in an aggregate state with a size region from 100 to 400 nm. This indicates that the dispersion and stabilization of C60 aggregates by humic substances can lead to the water solubility enhancement of C60. Comparing humic acid with fulvic acid, the water solubility enhancement of C60 by humic acid was about 10 fold larger than those by fulvic acid. The UV-Vis difference spectra for the humic acid solution containing C60 showed an absorption band at around 337 nm, while it was not observed for fulvic acid solution. These results imply that the charge transfer interaction as well as the surface activity of humic substances might contribute to the solubility enhancement for C60. These findings demonstrate that humic substances can play a fundamental role in transportation, reaction and biological toxicity of C60 in natural environments.

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Coagulation and fractionation of dissolved iron in estuarine mixing zone: the role of aquatic humic substances

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Dissolved iron in river water is one of the iron sources in seawater, and can play an important role in the bio-productivity in marine environments. However, the bio-productivity can be strongly controlled by the fate of dissolved iron in estuary. Previous reports have shown that over 90% of dissolved iron is removed in the estuary by the coagulation and the iron has a colloidal dimension of submicron size. On the other hand, slightly amount of dissolved iron ($^{10\%}$) can lead to the transportation into the marine environments, and can affect the bioproductivity. However, there is no information on the form of the stable iron in estuary. In aquatic environment, it is well known that humic substances (HSs) can act as a ligand and a colloidal carrier for metal species. In addition, among the aquatic HSs fulvic acid has a higher charge density and a lower molecular weight than those of humic acid. These findings imply that the aquatic fulvic acid can contribute to stabilization of iron at high salt concentration. In the present study, to clarify the role of aquatic fulvic acid we investigated the coagulation and fractionation of dissolved iron by mixing river water with artificial seawater. The size fractionation of iron in the river water was performed to identify the iron-fulvic acid complex. Moreover, fulvic acid was isolated from the river water, and was used for understanding the coagulation nature of the iron-fulvic acid complex. As the results, it was found that about 90% of the dissolved iron is removed and the remained 10% is stable in the seawater. The size fractionation of iron in the river water showed that the about 90% of the iron is distributed over the size range from 20 to 400 nm while a 10% of the remained iron is below 20 nm. The iron bound to fulvic acid isolated from the river water used was also distributed below 20 nm. The coagulation experiment for the iron-fulvic acid complex supported that the iron bound to fulvic acid can be stable in the artificial seawater. These results demonstrate that the fulvic acid can play an important role in the transportation of iron into marine environments.

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Surface thermodynamics studies on Biomass adhesion during expanded bed adsorption of bio products

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Cell disruption constitutes and essential processing step for yeast intracellular products, which is known to influence the quality of fluidization and the sorption performance in 'expanded' bed systems.

Cell electro-permeabilization coupled to direct product sorption on expanded beds contactors was explored. S. cerevisiae F17 was pulsated in batch mode (10 pulses, 1.5 ms, 4kV/cm, 2 Hz) and the properties of the resulting cell particles studied via surface thermodynamic approaches.

Several process-relevant observations were made: a) The enzyme utilized as model –glyceraldehyde-3-phosphate dehydrogenase, GAPDH- was released with high yield (87%) and good purification factor (1.5-2.0) in comparison with cell lysate as control; b) A shift in the surface properties of the cell particles was noticed e.g., the Z-potential changed from –12 mV to -9 mV upon pulsation while AB (γ + 3-4 mN/m, γ - 51-55 mN/m) and LW (28-30 mN/m) components suffered only minor change at pH 7; c) A reduced interaction of the electroextracted feedstock with DEAE-Streamline adsorbents was evidenced by the biomass pulse method i.e. cell transmission increased from 14% to 41% after pulsation; and d) the model product was purified by direct contact with a global yield of 59-76% and purification factor of \approx 12. Moreover, low protease activity was also observed i.e., < 20% of the activity present in the mechanically disrupted cell paste.

A novel primary recovery route for yeast intracellular bioproducts can be proposed by combination of selective permeabilization and immediate sequestration on a solid phase. This will translate in increased product quality, process yield, and cost-effectiveness.

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Uptake of heavy ions from residual water onto microgels

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Dispersions of microgel particles have recently been attracting a great deal of attention due to their ability to undergo large size changes in response to environmental conditions. Microgels are cross-linked colloidal particles that can swell by the absorption of many times their weight of solvent. From an applicability point of view, microgel particles can respond to environmental changes much faster than bulk gels due to their smaller size. Among them, temperature and pH have been the solution variables of greatest interest, primarily because these variables are important in physiological and biological systems. Thus, temperature- and pH-sensitive microgels offer opportunities for applications in heavy ions removal from aqueous systems for water purification.

Among these heavy ions, cadmium constitutes one of the most toxic one. Cadmium is found naturally on earth's crust in association with zinc, lead, and copper ores. Naturally a very large amount of cadmium is released into the environment. About half of this cadmium is released into rivers through weathering of rocks and some cadmium released into air through forest fires and volcanoes. The rest of the cadmium is released through industrial activities, such as manufacturing. Although its concentrations tend to be low in surface water, it is highly toxic at low concentrations and accumulates in biota.

The processes of cadmium containing water purification system with microgels are analyzed in this work. Thus, two different microgel with 10 wt% of N,N'methylene bis-acrylamide (BA, cross-linker) with respect to N-isopropyl acrylamide (NIPAM) were synthesized containing 0 and 10 wt% of AAc with respect to NIPAM. An environmentally friendly alternative is to treat CdCl2 containing water with microgels at good experimental conditions: the cadmium must be soluble in water (at low pH metals are in the dissolved form) and the acid groups of the microgels must be ionised (medium pH higher than the pKa of carboxylic groups). The attractive interactions between cations and anions make to absorb the cadmium into the microgel particles. The analysis of the supernatant by Atomic Absorption lets to know the amount of cadmium absorbed onto the microgel particles.

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Adsorption of MCPA on goethite and on Humic Acid coated goethite

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The sorption of the organic herbicide (2-methil-4-clorophenoxi)acetic acid, MCPA, on goethite and the ionic strength effect over that process was studied. Also, in order to simulate natural soil conditions, the interaction of MCPA with an association of humic acid, extracted from a soil from Galicia (NW Spain), and goethite was analyzed. In this way, the sorption of the anionic herbicide MCPA goethite $_{\mathrm{the}}$ binary on and on system was compared. Batch experiments were carried out at each experimental condition. After the sorption equilibrium was reached, the sample was filtered to obtain the free herbicide separated from the other reaction species. The MCPA-goethite sorption reaction was carried out at pH = 4 and at two ionic strengths, 0.02 and 8fr10-3 M in KCl. The MCPA-coated goethite sorption experiments were carried out at pH = 4 in 8fr10-3 M KCl.

The intrinsic sorption parameters were thus determined for the interaction of MCPA with goethite by the application of the surface binding model CD-MUSIC. In order to justify the sorption behaviour the participation of outer and inner sphere complexes was assumed.

On the other hand, the amount of MCPA adsorbed on the coated oxide was expressed as a function of the specific surface area of the synthesized oxide. It was found that the amount of MCPA adsorbed on the goethite sample was significantly higher than on the humic acid-goethite association. In this way it can be concluded that there is a decrease on the sorption positions that can be occupied by the anionic pesticide in the binary system in comparison with the goethite isolated fraction.

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A model for the impact of root exudates on the fate of heavy metals in the rhizosphere

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A mathematical model for rhizosphere processes, accounting for the impact of root exudates on the fate of solutes, is proposed. When only one exudate species is considered, three different species are subjected to transport in the unsaturated soil zone: (i) heavy metals (or the ions Mm+, respectively), (ii) exudates, as well as (iii) solute-exudate complexes. Besides convection and dispersion all species can underlie equilibrium and kinetic sorption, transformation-, degradation- or decay processes, and sources/sinks. A term accounting for the influence of exudates on (backward-) sorption reaction rates of heavy metals is also proposed as additional possible mechanism in order to produce higher amounts of free metal ions in the liquid phase. Processes such as complexation and ligand promoted dissolution are included, all based on recent experimental evidences. Microbial transformation of the organic ligands is implemented by assuming Michaelis Menten kinetics. As boundary condition for the Mm+-exudate complex at the root surface, a dissociation mechanism is assumed. The model can also easily be applied to simulate solute (e.g. nutrient) - instead of heavy metal - migration under influence of exudates. Certain plants under stress express higher amounts of root exudates, leading to an enhanced solute concentration around the root. Thus more appropriate conditions regarding nutrient supply may be created, or enhanced heavy metal uptake in the case of metal accumulating plants can occur. The proposed model shall reproduce the different concentration distributions at emerging exudates and lead to a better understanding of the relevant processes involved.

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Kinetics of Cr (III) adsorption on activated carbons

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The capacity of activated carbons for chromium (III) removal from aqueous solutions was investigated. The Langmuir and Freundlich adsorption models were used to represent the experimental data and equilibrium data fitted well to the Freundlich isotherm model. The negative value of ΔG[°] for Cr (III) indicates the spontaneous nature of sorption. Cr (III) is adsorbed due to the strong interactions with the active sites of the adsorbent. The kinetics data for chromium(III) adsorption onto activated carbon were studied according mass transfer and intraparticle diffusion models. A very good correlation coefficient was obtained using the pseudo-second-order kinetic model, suggesting that chromium (III) adsorption process on activated carbons tend to follow second-order kinetics.

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Electrokinetic properties of concentrated suspensions with biological contaminants

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Electrokinetic and dielectric properties are powerful analytical tools in colloidal science, being often used for the characterization of colloidal suspensions. This is why, theoretical models relating these phenomena to the system parameters have been developed in the last century. Among the studied systems, dilute suspensions of rigid spherical particles in suspension have a special significance, since they constitute the first approximation to real colloidal suspensions. This model and the associated boundary conditions was later extended to consider more realistic physical situations, e.g., rigid spherical particles with surface conductivity, spheroidal particles, spherical particles in concentrated suspensions, particles coated with an ion-permeable membrane, etc.

The analysis of the electrokinetic properties of colloidal particles coated with an ion-permeable membrane (soft particles) is especially important in many environmental problems. Several authors have developed theoretical models and have analyzed the behaviour of dilute colloidal suspensions of soft particles. However, it is well known that in the most of the interest practical situations the systems are concentrated in biological system. To our knowledge only Ohshima has presented an impressive series of papers in the last decade dealing with the electrokinetic properties of colloidal particles covered with a charged layer in a concentrated suspension. Although the semi-analytical solutions obtained in these works take into account the effects of the double layer polarization, their range of validity is limited, as is demonstrate in this work, to the cases when core radius tends to zero or when l(b-a) >> 1. Here b is the outer membrane radius, a is the core radius, and l is the ratio between the frictional coefficient of the membrane and the viscositv of the fluid. The aim of this work is to analyze the behaviour of the most important electrokinetic properties in concentrated suspensions of soft particles.

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Heteroaggregation of oppositely charged polymer colloids studied using Single Cluster Light Scattering

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Particle aggregation in natural waters is of importance with regards to particle transport, which has a significant influence on processes such as the formation of cohesive sediments and the transport of chemical species associated with particulate matter. Experimental evidence indicates that particle aggregation usually takes place among different colloid types (heteroaggregation). Aggregation of oppositely charged particles is usually referred to as electrostatic heteroaggregation. Here, we investigate the heteroaggregation using singlecluster light scattering (SCLS). This technique is capable to monitor the time evolution of the detailed cluster-size distribution (CSD) and the number average cluster size. Aqueous suspensions of positively and negatively charged polystyrene microspheres were used as experimental systems. The aggregation processes were investigated as a function of the electrolyte concentration and the relative amount of particles of opposite sign. At high electrolyte concentrations, the electric double layers surrounding the particles are completely compressed and the well-known diffusion limited cluster aggregation (DLCA) regime was observed. At low and very low electrolyte concentration, however, long range attractive and repulsive interactions become predominant and the corresponding cluster-size distributions show a quite interesting and unconventional behavior. In electrolyte free 1:1 mixtures, for example, clusters differing by only one constituent particle behave quite differently. This cluster discrimination phenomenon was already predicted by simulations and confirmed by experiments. Additionally, numerical solutions of the mean-field coagulation equation as well as Brownian dynamic simulations show that monomer discrimination is already observed when different reaction probabilities are imposed for the different types of possible monomer-monomer reactions.

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Effects of humic acid-oxide interaction on proton and metal ion binding to the complex of both colloids

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Binding of toxic metal ions at interfaces created by the presence of natural colloids such as humic substances (HSs) and metal (hydr)oxides is a key process that regulates the reactivity and transport behavior of these ions in soil and aquatic environments. For metal/colloid binary systems extensive binding measurements have been conducted, and sophisticated equilibrium models have been proposed to predict the binding over a wide range of conditions. However, in natural environments these colloids coexist and interact with each other. This affects the binding of target metals and results in deviations from the binding calculated with the binary models assuming additivity. Especially, the adsorption of the large molar-mass fraction of HSs, humic acid (HA), on oxide surfaces exceeds the limits of the conventional models. To improve our understanding of the processes that occur at oxide/HA/water interfaces the copper (Cu2+)/purified Aldrich HA (PAHA)/goethite (α -FeOOH) ternary system was chosen to investigate the effects of HA adsorption on metal binding. Copper binding isotherms to the PAHA/goethite complex were measured at different pH values, salt levels and HA/oxide ratios, and the isotherms were compared with the results obtained for the corresponding binary systems under similar conditions. The comparison revealed that Cu2+ binding in the Cu2+/PAHA/goethite ternary system was enhanced with respect to the sum of the binding in the Cu2+/PAHA and Cu2+/goethite binary systems. From the results of an analysis of the potentiometric titrations of PAHA-goethite mixtures, the increase of the Cu2+ binding was mainly attributed to (1) enhanced dissociation of protons from the functional groups of the adsorbed PAHA and (2) the change of the electrostatic potential in the vicinity of the goethite surface occupied with PAHA. As far as we know, it is the first time that the effects of HA-oxide interaction on metal binding are addressed with some chemical details. These findings certainly lead to the importance of taking into account the changes in both the chemical and the electrical states of the HA particles and the oxide surface, when one considers metal binding in metal/HS/oxide ternary system or in more complex soil and aquatic samples.

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Amount of aromatic compounds adsorbed

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The storage of domestic and industrial waste in sites of discharge can lead to serious problems of subterraneous water pollution due to infiltration of various percolates [1]. In order to avoid the contamination of phreatic sheets, it would be necessary to use geomaterial barriers very little permeable with interesting properties of retention towards inorganic and organic pollutants. In the present paper, we have prepared some geomaterials from the assembly of bentonite, silica, activated carbon and cement in different operative conditions. Retention properties of such barriers towards some volatile organic compounds (phenol, chlorobenzene and O-xylene) have been assessed through the determination of adsorption isotherms. Concentration of these organic compounds was measured by UV spectroscopy method. Kinetics of adsorption, effect of pH, initial concentration parameters have been examined.

The test achieved on the adsorption of some VOCs showed that this type of geomaterial exercises a good retention on the compounds aromatic as phenol, chlorobenzene and O-xylene. It demonstrates that this composite material is an efficient means of confinement of discharges of domestic and industrial waste.

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Assessment of the reactive surface area of the soil oxide fraction

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The speciation of metals and oxyanions in soil solution depends largely on their adsorption to the surface of soil components, like metal (hydr)oxides or clays, and their precipitation as separate phases. Our understanding of the binding of small ions to well defined mineral surfaces has increased in the last decade because of the development of surface complexation models (SCM). These mechanistic surface complexation models have been widely used to estimate the distribution of oxyanions and metals between sorbed and solution phases, as well as their ionic speciation.

Any application of these models to natural systems like water, sediments and soils require information on the reactive surface area involved in the adsorption process. The normal methods to determine the surface area of mineral surfaces, cannot be used to measure de reactive surface area of natural soils, as soils are heterogeneous systems in which part of the surface will be not reactive and inert in the adsorption processes.

A method is presented to derive the reactive surface area of soils. The method is based on the idea that the distribution of a well-chosen probe ion over solution and adsorption phase is determined by the reactive surface area in combination with binding properties. In the approach, the adsorption is calculated for wellknown conditions and combined with an experimentally obtained distribution to derive the effective reactive surface area.

The probe ion chosen in the method is phosphate since it binds predominantly to metal oxide surfaces. Moreover, phosphate is omnipresent in natural systems in relevant amounts and has been extensively studied in literature. Natural systems are multi-component witch implies that many interactions can influence the distribution between surface and solution. To simplify the system to conditions for which the interaction can be calculated, a high concentration of NaHCO3 as background electrolyte in the presence of Activated Carbon may be a good choice. The pH is buffered, the solubility of interfering cations (Ca2+, Mg2+) is suppressed and Activated Carbon may reduce the competition with natural organic matter. Under these conditions, the solution chemistry becomes dominated by the presence of the NaHCO3 that may interact with the adsorbed phosphate resulting in a phosphate desorption process. This desorption process is simulated and interpreted with a SCM taking into account the competitive CO3 binding, leading to an effective reactive surface area value for the soils systems studied.

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Interaction of pesticides with a surfactant-modified soil interface: Effect of soil properties

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Compounds from anthropogenic activities, such as pesticides, may cause environmental pollution, since they are applied to soil where they can remain or be transported to surface or ground waters. The surfactants may modify the retention and mobility of the pesticides and hence affect their environmental fate, because their transport will depend on their distribution between the soil solution and the solid phase. Batch tests with pesticides were carried out in soils with different physicochemical properties to which surfactant solutions of different nature were added. These compounds are introduced in the soil system through wastewater or by site-specific contamination. Soil organic carbon and cation exchange capacity were relevant parameters when cationic surfactants were added, since one of the main binding mechanisms is of electrostatic nature, through cation exchange. The physicochemical properties of the pesticides also played a role in the extent of retention, being the hydrophobic pesticides more retained than the polar ones.

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Ligand-facilitated reduction of uranium by Fe in aqueous solution

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Redox reaction of hexavalent uranium U^{+6} to tetravalent uranium U^{+4} plays an important role in predicting the migration behavior of actinides in geosphere. The solubility of U^{+4} is quite low, therefore the reduction of U^{+6} leads to retention of uranium. Fe^{+2} acts as a reductant of U^{+6} in nature. For instance, it is well known that the reduction of U^{+6} proceeds on the surface of iron (hydr)oxide. In contrast, it is widely known that Fe2+ does not reduce UO_2^{2+} in solution. This phenomenon is explained from their standard reduction potentials in solution. However, these potentials are influenced by co-existing ligands, and the reaction may proceed with existence of ligands. In the present work, we employed ethylenediamine tetraacetic acid (EDTA) as a test ligand. 10 mM UO_2^{2+} , 50 mM Fe²⁺, and 75 mM EDTA were mixed at pH 1.65 under argon atmosphere. The solution was analyzed by ultraviolet-visible absorption spectroscopy (UV-Vis). As a result, the peak of U^{+6} at 420nm decreased. Instead, the characteristic peaks of U^{+4} at 650nm, 550nm, and 480nm increased. This indicates that reduction of U^{+6} by Fe^{+2} is facilitated by co-existing EDTA. Other strong natural organic ligands such as carboxylic or amino acid most probably show same function as EDTA. We will present systematic studies of U^{+6} reduction by Fe^{+2} with several ligands existing in natural environment. This information will be of great importance for the safety assessment of uranium migration from disposed nuclear wastes.

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Removal of herbicides from water by static and dynamic adsorption on carbon materials

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Diuron and amitrole are group of hazardous compounds that may pollute surface and ground waters, due to their excessive use in agricultural activities, mainly used in olive tree plantations. Adsorption of these herbicides on activated carbon fiber, activated carbon cloth and granular activated carbon has been studied. Carbon materials were characterized to know their surface area and pore texture and their surface chemistry (surface oxygen complexes, acid base character, surface charge and hidrophobicity).

Adsorption experiments were carried out under static conditions at different solution pH, ionic strengths and temperatures. The effects of these parameters on herbicide adsorption were explained according to the speciation diagram, solubility, hidrophobicity and conformational analysis of herbicides and physical and chemical surface characteristics of the carbon materials. Adsorption kinetics of these herbicides on carbons as a function of adsorbent mass was also studied. From these experiments the external mass transfer and intraparticule diffusion coefficients were also determined.

Adsorption of pesticides was also carried out under dynamic conditions at 298 K in glass columns of 9 mm inner diameter, these columns were packed with different mass of carbons. A solution of the corresponding herbicide was pumped through the carbon beds at a constant flow of 2 mL min-1. From these experiments the breakthrough curves were obtained, and from these curves several characteristics of the carbon bed were calculated. The characteristics of the carbon beds have been related with the textural characteristics and the chemical nature of the carbon materials and with the chemical characteristics of pesticides. All carbon materials used in these studies show a higher adsorption capacity to remove diuron than that to remove amitrole due to the higher hydrophobicity of diuron.

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Adsorption of surfactants at the air-solution interface: theoretical description of adsorption equilibrium and kinetics

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The adsorption of nonionic surfactants at the air/water interface is generally believed to be diffusion-controlled and the model of Ward and Tordai is used to describe the time dependence of the surface excess. However, it was observed experimentally that, especially with surfactant molecules of a particular size and structure, diffusion is not the only mechanism controlling adsorption kinetics. In such a case the exchange kinetics of surfactant molecules between the surface and the layer adjacent to it (subsurface) also have to be taken into consideration. The importance of adsorption kinetics is manifested experimentally by an apparent lowering of the diffusion coefficient calculated from the adsorption kinetics data. This effect has been generally attributed to the existence of activation energy for adsorption connected with the need for orientation and reorganisation of the adsorbing molecules.

The objective of this work is to show how the concept of small associates formed by surfactant molecules in the interfacial layer can be used to interpret the equilibrium and dynamic surface tension data. The kinetic aspects of the adsorption are discussed on the basis of the Statistical Rate Theory, describing the interfacial transport in an isolated system. The diffusive flux between the sublayer and the region of bulk phase extending away from the surface is also considered. To derive the expression for the chemical potential of the surfactant molecules in the adsorbed phase an adsorption model is considered that allows formation of two-dimensional aggregates at the air/solution interface. In the model the adsorption layer is a mixture of monolayered disk-like aggregates of various dimensions, interacting via excluded area interactions. A four-parameter equation for chemical potential of surfactant molecules in the interfacial layer is developed, and next used in the SRT theory of interfacial transport to obtain the time dependence of surfactant adsorption. The predictions of the model are compared to the experimental equilibrium and dynamic surface tensions data of some n-alkyldimethylphosphine oxides. On the basis of the obtained results the role of 2D aggregation and the diffusional and transferring fluxes on the rate of adsorption are discussed.

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Co-adsorption of cationic surfactants and antioxidants on the hydrophilic silica surface

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Mesoporous silicas are a promising class of host materials for many biologically active substances. A number of recent studies have shown that the formation of surfactant structures at the silica/water interface may favour the uptake from solution of molecules which do not adsorb on the surface in the absence of surfactant. This phenomenon, called surface solubilisation, adsolubilisation or co-adsorption, concerns several areas of investigations such as pharmacy, cosmetics and environmental issues. The prevailing current view is that hydrophobic compounds are solubilised in the aggregate core, which possesses the properties of liquid hydrocarbon, whereas polar molecules are located in the palisade layer, where the solute-micelle interaction involves the predominant polar contribution.

The activity of many natural and synthetic antioxidants strongly depends on the local environment in which they act. For instance, in the micellar and microemulsion systems the rate of oxidation of hydrophilic ascorbic acid increases in the presence of cationic and nonionic surfactants and decreases in the presence of anionic SDS. The hydrophobic antioxidants such as carotene and -tocopherol, which are soluble in fats and not soluble in water, are much better stabilisers of natural fat products than less hydrophobic propyl gallate (PG).

The main goal of this study is to investigate the potential of mesoporous silicas as hosts for antioxidant immobilisation. To this purpose the adsorption isotherms of CTAB and CPC on the silica surface were determined and then the partition of various antioxidants in the two types of aggregates, i.e. bulk micelles and surface aggregates, has been investigated. The measurements were supplemented by the determination of the surface charge and zeta potential of silica particles in the presence and absence of surfactant. It was shown that in the case of hydrophobic antioxidants the co-adsorption effect is larger than the micellar solubilisation. At the same time the type of the surfactant polar head group was found to have a minor effect on the antioxidant partition.

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Colloidal characterisation of leachate from a contaminated retention pond sediment column

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The use of infiltration-retention pond to treat highway runoff water is a technical method developed for more than two decades [1]. Owing to sediment contamination, the groundwater pollution risk have to be evaluated [2, 3]. The maintenance of safe-driving conditions in wintertime needs the use of sodium chloride (NaCl) as de-icing medium. The study of runoff water salinity changes on the heavy metals mobilisation and release was investigated [4, 5, 6, 7] but few works deal with the specific colloidal fraction study. This paper gives the characterisation of "natural" colloidal material present in a leachate from contaminated retention pond sediment column. Sediment was leached alternately with NaCl to simulate the runoff of de-icing salt into the pond followed by rainwater. In series fractionation through filters and membranes was applied to the bulk outflow solution. Each fraction was analysed for major chemical elements, heavy metals and TOC. The UV absorbance of aliquots was measured for different wavelengths. The presence of humic and fulvic acids and high Zn, Cu, and Pb concentrations were highlighted. The investigations done by a set of imaging and spectroscopic techniques (SEM, ESEM, FFF-ICP-MS, MET and XPS) prove that Pb for example is strongly linked with particulate fractions. On the other hand, heavy metals such as Cd, Cr, Cu and Zn are mainly carried by various kinds of colloids. Main other result deals with the nature of colloids in function of their size distribution and trace element association. Colloids typically aluminium oxides, silicates, or humic substances are distributed in three major modes at 25 nm, 100 nm and 800 nm. Then, the concept of size based speciation or physical speciation [8] is clearly confirmed.

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Pollution-induced malfunctions of electrorheological fluids

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The phenomenon of Electrorheology (ER) is related to the changes in rheological properties of colloidal dispersions upon the application of external electric fields with a strength of several kV/mm [1]. Such changes are determined by an abrupt increase in the resistance to flow including, among others, a significant enhancement of the viscosity (up to several orders of magnitude) and the appearance (or magnification) of a yield stress [2]. It is generally accepted that the origin of the ER response lies on the aggregation of the particles in the suspensions (forming a more or less complex microstructure) that alter their rheological behaviour showing reversible liquidto-solid transitions in time scales of the order of milliseconds [3]. Because these mechanical properties can be easily controlled within a wide range, the ER fluid could be used as an electric and mechanical interface in various industrial areas. During the last decade, these potential applications have stimulated a great deal of interest both in academic and industrial areas in the ER field.

In this work, we investigate the possible modifications of the ER effect when a typical ER dispersion is polluted by different chemical compounds. It is well known that an ER suspension is generally made from an insulating liquid medium embodying either a semi-conductive particulate material or a semi-conductive liquid material (usually a liquid crystal material) [1]. However, this composition is sometimes altered by the presence of polluting agents which either may be accidentally included (for example, water) or may be intentionally added to improve the colloidal properties of samples (for instance, surfactants).

Contamination of these particular colloidal systems may produce undesirable polluting effects because of the required application of strong electric fields: a net decrease in the ER response, inadmissible power consumption, short-circuits, significant alterations of the working temperature. In order to evaluate all these possible malfunctions in an ER fluid, we have prepared a series of hematite/silicone oil suspensions, and we have determined its ER (viscosity and yield stress), electrical (current density) and thermal properties in the absence and presence of different contaminating additives: water, surfactants (Brij30)and plasticizers (tricresyl phosphate and dioctyl phthalate).

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Effect of dissolved silicates on uranyl adsorption on gibbsite

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Adsorption of toxic metal ions on metal (hvdr)oxide colloids or mineral surfaces plays an important role in regulating the toxicity and transport properties of these ions in subsurface environments. One of the examples is potential migration of radionuclides, such as uranyl (UO22+), from an underground disposal site to the biosphere surrounding us. So far, there have been many researches on the adsorption of radionuclides on metal (hydr)oxides, and the results have been tabulated mostly in the form of so-called distribution coefficients (Kd). The value of Kd for a given radionuclide/oxide pair depends on many factors including pH, ionic strength and the concentration of the target nuclide. The presence of other ions, that form stable complexes with the nuclide in the bulk solution or on the oxide surface, will certainly have a significant influence on the adsorption as well. Dissolved silicates species such as monosilicic acid (H4SiO4) are ubiquitous due to the dissolution of silicate minerals. They are reported to form stable complexes with UO22+ in the bulk solution and absorb themselves on oxide surfaces. Although these facts suggest that dissolved silicate ions may change absorbability of UO22+ considerably, the influences are not well-known. In this work the adsorption of UO22+ on gibbsite (Al(OH)3) in the presence of H4SiO4 has been investigated at various environmental conditions (pH, ionic strength, the concentration of UO22+ and that of H4SiO4). Silicic acid tends to form polymeric species in the bulk solution, which makes the interpretation of the obtained results complicated. This is tackled by differentiating the monomeric and polymeric silicates by the Molybdenum Blue or Molybdenum Yellow methods. The multi-layer formation of H4SiO4 on oxide surfaces is also reported and may affect UO22+ adsorption. Vibration spectroscopy can be used to identify the surface species of silicates and evaluate the change of UO22+ adsorption depending on the silicate loading on gibbsite.

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Concentration effects on transport of colloidal particles in unsaturated silica sand columns

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In this study, a series of experiments were conducted under unsaturated conditions using 0.8 μ m fluorescent microspheres and Pseudomonas fluorescence bacteria as tracers. Experiments were conducted using varying concentrations at approximately 80% saturation, in silica sand (570 μ m diameter, 0.39 porosity). The breakthrough of the colloids was measured in the effluent online and internally through the use of light fiber optic probes. The retention profiles were measured using fluorescent microscopy after sectioning. This technique allowed us to observe these different retention profiles, which show an initial exponential decrease followed by an increasing peak near the outlet. This behavior is deviant from that expected based on classic colloid theory. The results suggest that the initial concentration has influenced the retention within the column, due to a filtering effect such as straining. In addition, residence effects were studying by varying the flow rate.

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Decomposition of non-ionic detergents in water solutions and industrial sewage by advanced oxidation methods

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Surfactants constitute a big group of components that are generally used both in households and practically in all industrial branches and services. Their consumption in recent years has grown continuously, and as they almost do not decompose in the operations in which they are involved, they are removed wholly to the sewage.

In general, surfactants are not toxic for man and organisms living in water. Their negative interaction covers mainly a decrease of water surface tension, which facilitates dissolution in water of many toxic substances that usually can hardly be soluble or are completely insoluble in water. Their negative impact on self-purification ability of water reservoirs and development of biological life is also observed. Hence, it is necessary to develop effective neutralisation technologies.

An important group are non-ionic surfactants (NIS). Recently, a significant growth is observed in the range of their applicability and production. NIS s are the products of condensation of ethylene oxide with alkylphenols or long-chain alcohols. Surfactants, including non-ionic ones, which contain an aromatic ring, have usually low susceptibility to biodegradation, and in the case of polyoxyethylated alkylphenols reveal estrogenic action.

Technologies of purification of the wastewater that contains detergents must be multistage. Most frequently they include chemical or physicochemical and biological processes. Among chemical processes which have gained importance in the recent years, specially interesting are the processes of advanced oxidation. The authors present results of research on the decomposition of non-ionic surfactants in water solutions which is a result of various versions of advanced oxidation processes. Comparison was made between the oxidation efficiency of NIS solutions, especially of polyoxyethylated alkylphenols (Tritons) during ozonation, photooxidation, photo-catalytic oxidation and using jointly such components as ozone, hydrogen peroxide and UV irradiation. In the detergent decomposition also ionizing irradiation and Fenton s reagent. In all cases the process was optimised in relation to its basic parameters, i.e. concentration, time, temperature, oxidant dose and reaction procedure. An interesting factor was also the form of surfactant in the solution, namely whether aggregated forms (micelles) or monomeres (single particles) were predominant.

A factor important for the integration of chemical processes combined with biological purification, is the character and properties of formed products of oxidation, and in particular their biodegradability and toxicity of the solution. These factors were investigated using the analysis of biodegradability of the solutions measured as a ratio of biochemical oxygen demand to chemical oxygen demand (BOD5/COD). The analysis of solution toxicity was made with the use of microbiological ToxAlert test.

Results of investigations obtained in model solutions were used to verify the results of removal of the detergents from industrial wastewater. Such research was made for textile wastewater generated during washing of textile materials, for effluents from chemical plants that produce and distribute surfactants and car wash sewage. Textile wastewater purified with selected chemical methods was subjected to biological treatment using both active sludge and wetted bed.

The obtained results can be used to compare the purification efficiency of particular versions of advanced oxidation processes in relation to wastewater containing surfactants.

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Regeneration of activated carbon during biosorption purification of water from surfactants

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Recently the application of biosorption systems with granulated activated carbon (AC) for deep removal of organic substances from water is object of intensive researches. Especially urgent in these researches is the opportunity of AC bioregeneration. It can be carried out in a parallel mode of course of processes adsorption-biodegradation in one device. Question on, whether the substrate molecules in porous space are identical to initial substance or are exposed, in the certain measure, partial biodegradation was not found out. The purpose of the present work was to study of change of adsorbate structure in adsorbent supermicro- and micropores, which are not involved or partially are involved in process of spontaneous joint bioregeneration, and definition of an opportunity of complete AC regeneration after partial bioregeneration combined with sorption process.

As object of research the activated carbon KAU with the following structural adsorption characteristics was used: volume of micropores - $0.164 \text{ cm}^3/\text{g}$; a specific surface - $880 \text{ m}^2/\text{g}$ and the adsorption volume of pores - $0.51 \text{ cm}^3/\text{g}$. As an adsorbate ethoxylated nonylphenol (non-ionic surfactant NPEO) was used. The solution NPEO is filtered through biosorption system consisting from two adsorption columns, filled with AC .The biofilm in the first column was generated spontaneously owing to system non-sterility (KAU I). The AC in the second column previously was modified by microbes of a kind Pseudomonas (KAU II). After end of experiment carbon samples were selected from both columns and were processed by various procedures. The structural-adsorption characteristics of AC were estimated. Chloroform and ethanol solvents from carbon samples were used for quantitative definition of NĐEO homologues contents with a various ethoxylation degree by the method thin-layer chromatographyAs a result of spontaneous simultaneous bioregeneration process on the KAU I 0,20cm³/g adsorption pore space becomes free only. The whole volume of micropores (0,31 cm2/g) remains still occupied by the adsorbate. In the case of KAU II slightly more volume is freed - 0, 27 cm3/g. It is possible because small volume of microporous space is involved. As a result of carbon KAU I and KAU II washing by chloroform or ethanol some part of pores space is released additionally.

It is possible to conclude, that the carbon spontaneous bioregeneration, not modified by microorganisms, practically does not affect AC microporous space. It remains filled by NPEO homologues with a mainly low degree of ethoxylation. Extraction by chloroform allows in common with spontaneous bioregeneration to restore 58,8 % of porous space AC. At modifying AC by microorganisms a degree of bioregeneration AC and depth NPEO of destruction raise. The amount undestructed NPEO homologues in porous space decreases approximately in 2 times. The total degree of regeneration the AC after spontaneous bioregeneration and extraction by chloroform reaches 92%.

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Batch desorption studies and multiple sorption-regeneration cycles in a fixedbed column for cadmium elimination by protonated Sargassum muticum

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The protonated algae Sargassum muticum was employed in batch desorption studies to find the most appropriate eluting agent for cadmium-laden biomass regeneration. Eleven types of eluting solutions at different concentrations were tested, finding elution efficiencies higher than 90% for most of the desorbents studied. Total organic carbon and biomass weight loss measurements were made. The reusability of the protonated alga was also studied using a fixed-bed column. Eleven consecutive sorption-regeneration cycles at a flow rate of 10 mL.min-1 were carried out for the removal of 50 mg.L-1 cadmium solution. A 0.1 M HNO3 solution was employed as desorbing agent. The column was operated during 605 h for sorption and 66 h for desorption, equivalent to a continuous use during 28 days, with no apparent lose of sorption performance. In these cycles no diminution of the breakthrough time was found; although, a relative lose of sorption capacity, regarding the found in the first cycle, was observed. The slope of the breakthrough curves experiments a gradual increase reaching its maximum value for the last cycle tested (40%) greater than for the first one). The maximum cadmium concentration elution peak was achieved in 5 minutes or less, and the metal effluent concentration was always lower than 0.9 mg.L-1 after 1h of elution. The maximum concentration factor was determined to be between 55 and 109.

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The influence of the thickness of TiO2 nanocover on glass surface on the dependence of contact angle on solution pH

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The covering of the glass surface with the nanolayers of Ti02 was performed by means 6f molecular layering (surface synthesis). After 12 cycles of synthesis the samples with the layers of Ti02 amount from 1 to 12 were performed. The investigation of the dependence of contact angles (θ) on pH was made for these samples with the aid of microphotography of sitting drops. All the dependences B - f(PH) obtained were polyextremal, the position and pronouncement of the θ maxima being normally dependent on the number of Ti02 layers.

The B = f(PH) dependence measured for the initial glass was similar to that received earlier for quartz surface. The carrying out just one cycle of molecular layering of Ti02 significantly changed the wettability of the glass surface. As the number of the Ti02 layers increased the more pronounced θ maximum at pH region 5,5 - 6,0 (the pH value close to the zero point of the charge of Ti02) was observed.

In the process of Ti02 layering the next regularity was observed: the common (average) level of contact angles (8av) increased in the next consequence: from 1 to 4 layers and from 5 to 8 ones: at the transition from 4 to 5 and from 8 to 9 layers the θ av value sharply diminished.

The similarity of the common character of the dependences for samples with the number of layers n; n+4; n+8 (where n - the number of Ti02 layers from 1 to 4) was observed.

The results obtained permit in such a way to suppose that the discovered regularities of the changing the dependences of $\theta = f(PH)$ and θav with the change of the number of n02 layers are connected to the consecutive processes of formation at the glass surface the structure cell of anathase.

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Effect of temperature on surface tension of binary solutions of polyethylenemine

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Conditions of using surface-active polycomplexes constantly change with industrial processes. Defining the dependence of effectiveness of using polycomplexes on fluctuation in temperature and other factors of real medium makes this research of interphase layers of surfactant-polymer actual. The influence of temperature on the surface tension of their aqueous solution was analyzed in order to define the thermal stability of interphase layers of polycomplexes. The decrease of surface tension of binary solutions of anion surfactant-polybases was studied depending on time at various temperatures. It is shown that the rate of regulation the equilibrium conditions of mixed adsorption layers surfactants and polymers is increased by increasing the temperature.

The injection of micelle-formative surfactant to aqueous solutions of PEA and TETA increases the surface activity. It can be explained that there is a formation of mixed layers of surfactant-polymer between the two phases and appearance of associates. Calculation of thermodynamical parameters showed that the formation of adsorbtion layers occur with entropy profit. Entropy character of adsorbtion has some importance in structures of solvent and it means that destruction of "iceberg" structures of water surrounding the hydrocarbon radicals of surfactant ions when these radicals came out to boundary phase of adsorbtion. Adsorbtion of polycomplexes of PEI - DDS has less entropy profit than separate components. Tl[~]e decrease of entropy change of adsorbtion of complexation is explained by causing strong intramolecular cohesive force which is compatizing with macromolecular PEI - DDS associates. It limits differentiation of segments on surface activity in adsorbtion layers. Synergetic effect of surface tension in binary solutions of PEI - DDS is decreased by decreasing temperature. Composition of interphase of adsorbtion layers of associates of PE I - DDS nS on boundary division of liquid-gas was calculated first time. It is found that the ratio of PEI/DDS nS in interphase layer is more than n v in solution. This proves that complexation occurs more in boundary phase than in volume and as a result hydrophobizated interphase polycomplex with big amount of hydrophobe is occurred.

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Observing network structures at water-silicon wafer interface by AFM

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It is well established the basic role of water in any process in which material surfaces are exposed to environmental conditions. Therefore, it is of central interest to go deeper inside the water behavior at any scale, specially down to nanometer scales. To this purpose, we have explored how the water behaves in the nano-scale on a silicon wafer substrate, that is an important support in electronic industry and whose ultra-flat topography makes it optimal to be used as a substrate for nanometer-scale research by AFM. Recently, different objects (small dots and islands, network structures) have been captured on mica, which is another model substrate for AFM analysis, in air-ambient conditions after treated with pure water. They were thought to be condensed water in a novel arrangement. In this work, images of network structures at the water-silicon wafer interface with similar characteristics to those found on mica are presented. The effect of environment conditions (temperature, humidity) on these topographical features has been studied.

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Dewetting at Water-Silicon Wafer interface at the nano-scale by AFM

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Nanowetting of materials is important to clarify different phenomena in chemistry, electrochemistry and biology (e.g., atmospheric corrosion mechanism, wetting alterations of mineral surfaces due to asphaltenes in crude oil, adsorption behaviour of proteins and surfactants). Nano-scale exploration of wetting/dewetting phenomena at water-silicon wafer interface, an ultra-flat surface showing nanometer-sized roughness, should give rise to a better analysis of the surface hydrophobicity at smaller dimensions than usual macroscopic techniques. This would help to a better understanding of the adsorption behavior of contaminants and surfactants, whose sizes are usually in the nano-scale. Water micro- and nano-droplets and films have been observed using non-contact AFM, and their distribution with respect to surface features has been discussed. Phase imaging has been used to get insight into the physical nature of the different structures observed, and nanodroplet profiles have been analyzed to calculate contact angles from nanoscopic techniques, which have been compared to those coming from contact angle goniometry.

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Oxidizer influence on the formation process of primary (nanosized) particles in the Fe-H₂O-O₂ system

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The processes running in the system $\text{Fe-H}_2\text{O-O}_2$ are in the base of the galvanocoagulation method for technogeneous solutions of galvanic plants purification from heavy metal cations. During the formation of ultradisperse (nanosized) iron oxides and heavy metal ferrites the cation sorption from solution by iron monohydrate phases and the transformation of their structures with the involvement of the solution components in the crystallization occurs. The obtained compounds are characterized by the biological and chemical inertness and can reliably compact dangerous components preventing a contamination of the environment.

The aim of the present investigation was the study of the influence of oxygen access on the formation of primary nanosized iron-oxygen structures and their subsequent transformation in the Fe-H₂O-O₂ system.

For the process modelling the laboratory disk plant (St3) the iron disk of which conditionally was divided into four sectors two of them provided the contact between iron and carbon, other two represented iron surface without galvanocontact was used. The disk rotated for five days and nights in distilled water and then it was stopped and stayed motionless more three days and nights during which the transformation and formation of the iron-oxygen phases in the air and in solution passed.

The phase-forming process on the iron surface under the conditions of free access of the air oxygen. The nucleation of the iron-oxygen structures on the disk surface is associated with the process of its ionization with the formation of Fe2+ ions. The interaction of Fe2+ with the air oxygen results in the formation of Fe(OH)2, first, and the primary nanosized particles of protolepidocrokites [Fe22+Fe13+Ox(OH)2](7-2x-y)+;[Fe12+Fe13+Ox(OH)y](5-2x-y)+, then. The transformation of the latters accomplishes by the fL-FeOOH lepidocrokite formation predominantly, capable to enter into the interaction with solution components with the formation of iron ultradisperse oxides and monohydrates of different modifications, in particular, goethite and in the availability of heavy metal cations of the corresponding ferrites.

The phase-forming process in the galvanocontact iron-carbon under condition of free air oxygen access differs that the Fe2+ cations entered in the system are oxidized, hydrate, and hydrolyze rapidly with the formation of three valent iron hydroxoaquacomplexes. The nanosized particles of ferryhydrite 5Fe2O3.9H2O, which further is transformed into fÑ-FeOOH, transferring into fÑ-Fe2O3 or Fe3O4, is primary product of the phase forming process.

The transformation of iron-oxygen structures on the iron surface and in galvanocontact iron-carbon in the absence of free air oxygen access. The transformations of the ironoxygen structures on the surface of iron immersed in solution take place by the way of the rearrangement of protoproducts - ferryhydrite and protolepidcrokites and goethite phases as well as lepidcrokite in Fe3O4 magnetite.

Thus, it is shown that under limited air oxygen access the formation of the condensationcrystallization type structures, which are able to retain the compacted components of solution in crystalline lattice, took place. Such conditions are realized in practice during the galvanocoagulation process in the apparatus of drum type (galvanocoagulators).

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Systematic Synthesis and Property Examinations of Lithium Carboxylates Scaly Crystals for Candidates of Water Remediation and Environmental Improvement

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There have been developed and utilized many kinds of surfactants, for micelle formation, emulsification, dispersion, gel formation, and for other purposes. Some surfactants are effective for emulsification, and others for micelle formation. However, only through the way of preparing each surfactant for each purpose, it is rather difficult to understand the relationship among structures and properties of surfactants and functions and utilities of necessity. Especially, when we want to utilize surfactants for the purpose of remediation of oil polluted water, it is necessary to understand and change systematically physicochemical properties of surfactants and have to fit for each situation of pollution, because there are many kinds of oils as pollutants and many kinds of polluting situation. In this paper, as the typical surfactants for systematic analysis of physico-chemical property changes depended on alkyl chain length, we selected one of the simplest and safe surfactants, which have been used for a long time on the earth, a series of lithium carboxylates with straight alkyl chain, from carbon number 8 (lithium octanoate, C7H15COOLi, C08Li) to carbon number (lithium docosanoate, C21H43COOLi, C22Li). 22 All these lithium carboxylates were synthesized in aqueous and alcoholic solutions at 40 to 150 degree C under atmospheric to 1MPa pressure, in glass vessel with electric heater and powerful magnetic stirrer. Each surfactant was pure by elementary analysis, and very thin and scaly crystal structure, each leaf was thinner than 100nm by SEM observation.

Physico-chemical properties of these carboxylates were measured and analyzed. Solubility in water changed drastically depended on alkyl chain length. From C08Li to C10Li, solubility was very large, and in case of more than C18Li, practically insoluble at room temperature. By DSC analysis, C09Li to C22Li showed two step clear melting phenomena, however C08Li showed only one high temperature melting. In case of C09Li to C22Li, lower melting points were among 30 to 150 degree C depended on carbon number, and when each carboxylate was heated to just lower than high melting point, the lower melting could be reproduced repeatedly. However, once heated to higher than higher melting points, both lower and higher melting phenomena could not be reproduced again. These results showed only alkyl chain loosened during lower melting process, and fundamental scaly crystal structure did not change at all.

By DSC and XRD analysis, typical odd-even effect was observed. XRD pattern of odd number lithium carboxylates were resembling with each other, and much different from even number groups. Lower melting temperature of C09Li is 38 degree higher than C10Li, and enthalpy change of melting of C09Li is more than 3 times that of C10. These odd-even effects decreased as the carbon number increased, but the tendency was clear to higher carbon numbers. Other systematic properties will be shown also.

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Adsorption of micelle forming and non-micelle forming surfactants on the adsorbents of different nature

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According to the developing considerations water-purification is a part of mineralization processes of man-caused property, which is inclusion of vital functions products, waste and metabolites into the continual natural cycles of substance and energy exchange. Study of water-soluble organic substances adsorption in order to find effective and cheap adsorbents both natural and artificially created is the relevant problems of the XXI century. In connection with the increasing use and global scale of production of detergents being pollutants of water bodies, grounds and soils in this paper absorption of both micelle-forming surfactants - components of detergents (anionic sodium dodecylsulfate - SDS, cationic cetyltrimethylammonium bromide - CTAB, nonionic Triton X-100 and non-micelle-forming surfactants -aliphatic alcohols (n.-butanol and n.-pentanol) on aluminum oxide (chemically pure) and schungite was studied. Middle homologues of alcohols may be used as foaming agents especially to form non-stable foams in flotation. Alcohols adsorption was also studied on the following adsorbents: bentonite, near Moscow loess, Podolsk limestone, Vladimir dolomite, sawdust, sulphate lignin (by product of pulp and paper industry), and shales. Isotherms of adsorption and the values of maximum surfactants adsorption on the studied adsorbents were obtained according to the data of surface tension by Gibbs-Langmuir equations. Critical micelle-formation concentrations of the solutions of surfactants were determined by tensiometric and conductometric methods. For thermodynamic estimation of adsorbents efficiency the standard Gibbs free energy of adsorption and standard Gibbs free energy of micelle-formation was calculated. Comparison of these two values for micelle-forming surfactants enabled to conclude that sewage treatment from cationic CTAB is possible on both powders of schungite and aluminum oxide unlike anionic SDS for which aluminum oxide is not efficient. The most effective polar and non-polar adsorbents are revealed for alcohols. The given results on surfactants adsorption, in particular on aluminum oxide, are interpreted on the basis of E.A. Nechaevs conceptions (1989) on connection of adsorption ability of organic molecules with resonance potential of adsorbents. The obtained conclusions are discussed in connection to ecological problems of the Lake Baikal s basin.

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The role of surfactants for the stabilization of oil magnetic suspensions

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Unprocessed oil wastes are thrown to the environment mainly because of the difficulty of their recycling. In order to recycle these wastes the control of the aggregation processes in oil suspensions is required. In this work, we describe different methods for the stabilization of oil magnetic suspensions containing iron or ferrimagnetic metal oxides. These suspensions are usually called magnetic fluids and they can be classified into two main categories: Ferrofluids (FF) and Magnetorheological Fluids (MRF). In the case of FF, the average particle diameter is 10 nm and, therefore, the thermal energy prevents particle sedimentation or aggregation induced by magnetic attraction, although it does not avoid coagulation due to van der Waals forces. Therefore, the use of adequate surfactants is needed to overcome this problem [1]. In MRF, high density magnetic particles of an average diameter of 1 micron are dispersed in low density oil carriers and, in consequence, the suspensions suffer from excessive gravitational settling, which significantly difficult their recycling. This work is devoted to the effect of surfactant addition on the stabilization of FF and MRF, and the stability of magnetic fluids composed by micron-sized magnetic particles dispersed in ferrofluids, that is, MRF with an extremely bimodal particle size distribution [2].

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Redispersion phenomena in iron/oil suspensions

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The redispersibility of sediments in oil wastes plays an important role in the recycling potential of these wastes, which otherwise are thrown to the environment. In this work, the effect of three different additives (oleic acid, aluminum stearate, and silica nanoparticles) on the redispersibility of concentrated iron-based suspensions is investigated. With this aim, the redispersibility was studied, in a quantitative way, by means of rheological measurements, both in the presence and in the absence of external magnetic field. For this purpose, samples were subjected to a constant shear stress at different moments (steps) of the settling process. The time evolution of the corresponding shear rate was measured at each step. Interestingly, it was found that although the addition of oleic acid or aluminum stearate does not avoid particle settling, the redispersibility of the suspensions is considerably enhanced. On the contrary, silica nanoparticles behave as a gel-forming agent capable of preventing particle settling under rest conditions. Unfortunately, when ironsilica suspensions are sheared compact sediments are progressively formed, making the redispersion extremely difficult.

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The electric response of polystyrene particles dispersed in heavy ions solutions

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The aim of this work was to study the change observed in the electric behaviour of colloidal particles when these capture heavy ions. The electric behaviour of the samples was analyzed from their dielectric dispersion spectra obtained measuring their impedance from 20 Hz to 1GHz. In order to determine the change in electric response owing to heavy ions, the dielectric spectra of colloidal suspensions in La(NO3)3 y KNO3 were analyzed comparatively. The concentrations of electrolyte in which the particles are effective capturer of ions have been determined. The influence of the concentration, charge, and size of the particles on this process was also analyzed.

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An experimental method to measure the stability of concentrated colloidal suspensions

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The recycling of oil wastes and suspensions is nowadays one of the main challenges of the automobile industry, not only because of the evident economical cost but also, and more important, due to the severe ecological problem involved. The main difficulty for the processing of these concentrated suspensions is the sedimentation of their solid phase. Sedimented dispersions become useless as lubricants or driving fluids in shock absorbers, clutches and brakes when the appearance of solid residues takes place. For these reasons, it is necessary to get a better understanding of the sedimentation of particles in concentrated suspensions in order to improve their stability. Although several procedures have been proposed to study this problem, none of them is completely reliable. In particular, optical measurements are also hard to perform, since the presence of polluting metal particles makes these samples completely opaque.

In this work, we propose an alternative method to determine the stability of the suspensions: the measurement of the changes in the inductance of one or more coils surrounding the tested samples. When the sedimentation of particles occurs, the permeability of the different regions of the sample changes, decreasing at the top and increasing at the bottom of the dispersion [1]. As it will be demonstrated, this method provides important advantages. It is a non-intrusive technique, the concentration of particles is not a limiting factor, and it allows to also determine the particle concentration profile along the entire suspension. This will be shown experimentally using iron/mineral oil suspensions as models of typical polluted lubricant agent. The sedimentation rate and the iron particle concentration profile are studied as a function of the solid content and time. The obtained results reflect the reproducibility and precision of the proposed measurement device.

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Wetting on model heterogeneous surfaces from two points of view

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After recent ecological disasters such as those caused by Erika and Prestige and the Kyoto convention in full effect, world environmental politics is changing. The increasing worry by the sustainable development of actual society forces to develop new environmental-friendly technologies as well as novel cleaning techniques.

Processes with moving contact line are crucial for many applications in detergency and oil spills clean-up. The oil-drop detachment from a solid surface is mainly originated by a wettability alteration. The most interesting solid surfaces usually reveal a moderate heterogeneity. In this sense, the influence of surface heterogeneity on contact angle plays a determining role for a successful oil-removal.

Any drop deposited on a heterogamous solid surface exhibits a nonaxisymmetric shape. This asymmetry involves a multiplicity in contact angle which is defined by more than a simple mean value.

Status quo in the field of interfacial techniques aimed to wetting phenomena, in particular the sessile drop method, continues being limited to approximations of spherical caps and axisymmetric shapes. With these approaches, one only side view of drop is required. As alternative, we propose the simultaneous acquisition of top and side views of the sessile drop. From two or even three images, we can characterize the wetting of a drop using an average contact angle and the extremes values of contact angle. Axisymmetric Drop Shape Analysis-Diameter (ADSA-D) and Axisymmetric Drop Shape Analysis-Profile (ADSA-P) were used to analyze each drop images. This approach was tested by simulations with Surface Evolver which allows to obtain the complete range of local contact angles from the same input parameters than ADSA-D.

In this work, we used acetate surfaces with different heterogeneous patterns obtained from a high resolution laser printer. Light confocal scanning microscopy was used to characterize the topography of these surfaces. The irregular shape of drops was correlated to each heterogeneity pattern through their geometrical compactness.

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Effects of floc size and volume concentration on the settling of floc suspensions

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Flocculated clay suspensions at high volume concentration have been well known to settle firstly at a slow constant velocity and subsequently at a rapider velocity after a few ten-minutes. In this phenomenon, Michael & Bolger gave the experimental equation for the effect of volume concentration on the velocity in the rapid stage. However, this equation is built up by adopting the assumption that each of settling floc has a constant size regardless of volume concentration. Actually, there is a clear difference between floc size obtained from the final sedimentation volume and floc size obtained from M&B's equation. So we investigated the effects of floc size and volume concentration on the settling of flocculated clay suspension by a more accurate experiment, and derived the equation for settling velocity as a function of floc size.

The obtained results were as follows:

(1) The slow settling process becomes longer as the size of floc increases, and the settling rate in the rapid settling process increases with increase of floc size. In addition, the sedimentation volume increases with the increment of the floc size.

(2) The floc diameter increases at the same volume concentration when the flocculation is promoted by the addition of organic matter and stirrer agitation, and this fact has remarkably appeared in the experimental result of the settling.

(3) We defined the initial sedimentation volume as a sedimentation volume in point of time in which the rapid settling process ended. The defined sedimentation volume reflects the size of settling floc in the rapid stage. The floc size obtained from the initial sedimentation volume decreases as the volume concentration increases.

(4) Assuming the self-similar structure of floc, we proposed a new settling rate equation for rapid settling as a function of floc size and concentration. The rapid settling velocity obtained by the new equation (fractal dimension 2.35) agrees well with measured values. Furthermore, the proposed equation gives a clear explanation of experimental results $(1)^{\sim}(3)$.

(5) The measurement of settling rate is shown to be an useful method to determine accurately the structure and size of floc.

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P59The tribology role in the reduction of environmental noise and dust pollution

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The design, the production and the maintenance of road and railway vehicles are involved in restrictive environmental normative and demands, imposing to the European companies a meaningful improvement of the performances, reliability, but, above all, of the environmental respect; such target is surely achievable by a constant technological innovation policies. The aim of this paper is to underline the objectives of the tribology investigations activities in order to improve the railway and automotive tribosystem design for the environmental purpose, in terms of mechanical efficiency, noise pollutions, and dust pollution (wear resistance). After an introductions on the most meaningful theoretical and experimental results achieved by numerous researches, we present some results obtained at the DIMEC of Salerno on the brake tribosystems investigations.

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Effects of pH and H_2O_2 concentrations on treatment of leachate by using electro-femton methods

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Leachate is classified as strong wastewater and it is hardly treated, therefore it is the most significant problem for landfilling of solid waste. The amount of organic and inorganic substances included in leachate varies with respect to the age of landfill and the type of solid waste. In past, anaerobic and aerobic methods were generally applied for the treatment of strong waste water such as leachate. However, the difficulties of the applications and relatively low treatment efficiency for these methods direct researchers to alternative methods. These alternative methods utilize advance chemical and physical treatments. Besides, there is an increment on the application of electrochemical treatments of wastewater. It is reported in literature that the electrochemical methods are applied very efficiently to the treatment of the wastewater from textile and oil industries, which include hardly decomposed and toxic organic pollutants.

Electro-Fenton is a hybrid electrochemical method. In this method; organic materials in wastewater are removed synchronously by using Fenton oxidation, electrochemical oxidation and electro-coagulation. In this paper, the treatability of leachate by using Electro-Fenton method was investigated. In the experiments, the samples were taken from the leachate of the landfill of Sivas City (Turkey) before discharging into Kizilirmak River. The samples were filtered with filter paper to remove coarse substances. Then, the samples were processed within Electro-Fenton reactor having cast iron plates, under 2 Ampere DC current, various pH and H2O2 concentrations for a total of 45 minutes. The grabbed samples were taken at the times of 0, 5, 10, 20, 30 and 45th minutes. By analyzing pH, EC, COD and color, Fe(II) and Fe(III), the removal efficiency of this method was determined. In addition, the removal of nitrogen and phosphor were observed by the measurements and analysis of the grabbed samples at the time of 0 and 45th minutes.

Based on the results of our measurements and analysis; in case of the 2 Ampere DC current, the most efficient treatments were achieved within the values of 2 and 4 for the initial pH. Besides, it was observed that the efficiency of the treatment increased with the increment of the H2O2 concentration. However, the acceleration of the increment for the efficiency reduced for the high H2O2 concentration. Under the optimum process conditions (i.e., initial pH=3, treatment time = 20 min., the concentration of H2O2 = 2000 mg/L), 70% COD and 90% color removal were achieved for the leachate. It was observed in the experiment that at the end of 45 min. for the treatment time period, NH3-N and PO4-P removal were 80% and 25%, respectively.

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P61 Study of the second kind electrokinetic phenomena by means of the network method

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The colloidal science comprises a very large world: there are a lot of systems in nature whose study suits with it. Inside this group of systems, some of the most interesting ones are those related with the environment. In this sense, a good knowledge of dielectric and electrokinetic properties of colloidal suspensions is desirable to do more efficient some processes such as purification of water, remediation of soils and others.

Dielectric and electrokinetic properties have been widely studied using different techniques such as dielectric spectroscopy, electrophoresis, electrorotation and dielectrophoresis. Although all the mentioned techniques have been studied using theoretical and experimental methods, where numerical methods were applied, only first kind approach was considered, under the supposition that this would be a good approximation for low electric external fields applied.

In this work we use the network simulation method to solve the equation system governing the second kind electrokinetic phenomena. The network approach makes it possible to obtain the solution for this problem without any restrictions on the values of the parameters such as intensity of applied electric field, number of ionic species, etc.

The method consists in establishing the similitude between the mathematical model of the considered problem and that of an electric network designed in such a way that it has the same balance and constitutive equations. The original problem is thus reduced to the solution of a circuit (i.e., determination of currents and voltages), which is done using an electric circuit simulation program. Highly developed commercially available software for circuit analysis can thus be employed to obtain the dynamic behaviour of the system, without having to deal with the solution of the governing differential equations. The methodology is simple because only a few branch elements (resistors and current sources) are necessary, which are connected in such a way as to fulfil Kirchhoff s laws for currents and voltages.

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Anisotropic aggregation in aqueous suspensions of magnetic colloids

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Aggregation of magnetic colloids plays an important role in environmental processes such as water treatment or magnetic separation techniques for clearing polluted media. The aggregation behaviour of colloidal systems is mainly controlled by interparticle forces. Dispersions of magnetic particles are a special case of colloidal systems in which anisotropic magnetic forces are present in addition to the classical isotropic van der Waals and electrostatic forces. In this work, we study the influence of the additional anisotropic interactions on the aggregation behaviour of the particles as a function of their relative strength and importance. The aggregation kinetics and the spatial structure of the clusters formed were assessed by means of static and dynamic light scattering. In presence of an applied magnetic field, even relatively small changes in the electrostatic interactions were found to have a strong effect on the aggregation kinetics. The cluster structure is, however, mainly controlled by the strength of applied magnetic field. A qualitative explanation in the framework of the extended DLVO theory is also proposed.

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A clay-vesicle system for water purification from organic pollutants

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Water treatment technologies for removal of organic pollutants include methods micellar-enhanced ultrafiltration, flocculation-precipitation, such asoxidation/reduction, chlorination, etc. The use of granular activated carbon in fixed bed columns has become the most widely-used method. A clay-vesicular system was designed for testing the removal from water suspensions of the herbicides imazaquin, atrazine, alachlor and sulfentrazone. In a first procedure, montmorillonite at a clay concentration of 5 g/L was added to suspensions of vesicles of didodecyldimethylammonium (DDAB) preincubated with the herbicide solutions. The vesicle concentrations used were 3 and 6 mM. Appreciable percentages (>75%) of the added amount, 10 mg/L of removal were achieved for the anionic herbicides imazaquin and sulfentrazone, and for the neutral herbicide alachlor. However, the removal of atrazine was very poor for the lowest DDAB concentration, and a 2-fold increase in the concentration of the organic cation only enhanced 0.6-fold the percentage of removal of this herbicide. The removal from solutions containing two herbicides showed that the presence of alachlor molecules produces a synergistic effect on the binding of atrazine molecules to the DDAB vesicles, yielding an increase in its removal. In a second procedure, removal of herbicide from water solutions was performed by adding a prepared DDAB-clay complex at the same ratio as used in the previous experiments. The percentage of removal of the herbicides increased with respect to the previous procedure except in the case of alachlor which was somewhat smaller. An additional experiment was performed where the removal of herbicides from a solution containing simultaneously the four herbicides was compared to the removal by activated carbon. The efficiency of the clav-DDAB complex for removal of pollutants was significantly larger than that of activated carbon.

A column filter filled with a mixture with sand of either DDAB-clay complex or activated carbon was constructed and examined for the removal of the herbicide sulfentrazone. A solution of sulfentrazone was passed continuously through both types of filters. A 5:1 ratio between the volumes added to the filter containing clay-DDAB and activated carbon, respectively, was obtained for a 63% capture of the herbicide.

In summary, these results show the advantage of using a clay-DDAB system for water purification versus more traditional technologies, such as adsorption by activated carbon.

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Time-dependent sorption of norflurazon in four different soils. Use of bcyclodextrin solutions for remediation of pesticide-contaminated soils

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The photochemical behaviour of the herbicide norflurazon in the presence of different colloidal components of the soil and several cyclodextrins (CDs) has been investigated. The selected colloidal components were: a natural metal-fulvic acid complex, two synthetic humic acids, three different standard clay minerals (illite, kaolinite and montmorillonite), a synthetic acicular goethite, and natural clay fractions extracted from two different soils. The CDs employed were: beta-cyclodextrin (BCD), hydroxi-propyl-beta-cyclodextrin (HPBCD) and methyl-beta-cyclodextrin (RAMEB).

The interaction of norflurazon with BCD, HPBCD and RAMEB yielded the formation of inclusion complexes at a 1:1 stoichiometric ratio in solution. Apparent stability constants of 360.16, 359.47, and 558.51 M^{-1} and an increase in herbicide solubility by up to 5-, 35- and 54-fold for BCD, HPBCD and RAMEB, respectively, were obtained from the phase solubility diagrams at 25 °C in water.

In general, the presence of the different soil colloidal components in aqueous suspension provoked the reduction of norflurazon photodegradation rate, which followed a first-order kinetic. In contrast, the presence in such systems of the different CDs selected showed an inductive photodegradation effect on the herbicide, which could be mainly assigned to the inclusion effects of CDs to catalyze interactions between norflurazon and certain reactive radicals generated by the different colloidal components. In conclusion, this work reveals that the effect of the CDs on the herbicide enhanced solubilization coupled to an increased photodegradation could be a promising method for pesticidecontaminated soil remediation.

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Limit between dilute and concentrated suspensions of contaminants

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The colloidal suspensions and their applications are largely known. They are present in our every day life, supposes a multitude of uses: environment, biology, industry, medicine, engineering, etc. In particular, some environmental applications are: knowledge of the behaviour of contaminants in water, atmosphere and soils; treatment of wastes; water purification; decontamination of soils; reduction of the emissions and decrease of the concentration of pollutant colloidal particles in the air, etc.

Most of these applications depend on the zeta potential, ζ , of contaminant particles, and for many years a lot of empirical expressions have been obtained relating this parameter with the specific application. However, this qunatity cannot be measured, so it is necessary obtaining it indirectly by means of the electrokinetic properties of system. Therefore, theoretical models are necessary to establish a relation between the experimental measurements and the ζ potential. Dilute suspensions of rigid spherical particles are a first approximation to reality. This standard model has been extended to consider more realistic physical situations such as concentrated suspensions.

It is important to consider the limit between dilute and concentrated suspensions to decide the best theoretical model that must be used. This limit has been studied in different papers in the last years. However, in all these works it has been assumed that the diffusion coefficients of counterions and coions are identical. In recent papers it has been shown, for dilute suspensions and for ac fields, that if the diffusion coefficients differ from one another, the electric double layer thickness extends as far as the diffusion lengths of the ions. This means that the overlap of electric double layers of different particles should occur for lower concentrations than it is considered classically. The aim of this work is to analyse the limit between dilute and concentrated colloidal suspensions taking into account this point.

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P66 Electrokinetics of polydisperse systems

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Although the interest of electrokinetic techniques in the characterization of colloidal suspensions of a great variety of compositions is out of doubt, there are fields where the requirements are so specific that the theoretical models in hand are of less utility. Ons of these fields is the industrial applications (pharmaceutical products, paints, ceramics, etc) where not only the suspensions have typically high solids concentrations, but also comprise particles with a broad distribution of sizes.

Among the most suitable techniques for the study of concentrated dispersions are those based on electroacoustic effects (electrokinetic sonic amplitude, ESA, and colloid vibration potential, CVP). Existing models allow to obtain from the electroacoustic signal not only the size distribution, but also the dynamic mobility (ac counterpart of electrophoretic mobility).

In a previous work [1], we have determined the dependence of the dynamic mobility on volume fraction of solids in order to extract the zeta potential, surface conductivity or any of the parameters characterizing the electrical state of the interface. The theoretical predictions are based upon the numerical solution of the cell model equations for the case of monodisperse systems. Our aim in this work is to extend that theoretical formalism to polydisperse systems using the assumption that the particles size fit to a log-normal distribution. The results will be compared with experimental data obtained from ESA measurements.

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Evaluation of the performance of a solar photocatalytic reactor to disinfect water in field tests

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A recirculation solar reactor (SOLWATER) that uses heterogeneous photocatalysis and photosensitization was tested in a shanty house in the Province of Tucumán, Argentina. The present communication describes the main characteristics of the reactor and the results of the tests carried out. To evaluate the capability of the reactor to disinfect water, the concentration of four types of bacteria present in the water was followed as a function of the irradiation time and meteorological conditions. The chosen organisms were total coliforms, fecal coliforms, Enterococcus faecalis and Pseudomonas aeruginosa. The evaluation of the evolution of bacterial concentrations leads to the following conclusions:

(a)Neither time nor accumulated total energy defines per se the rate of bacterial destruction. Both factors must be taken into account. Also very important is the ratio (time under irradiation) / (total experiment time) (in the SOLWATER reactor, this ratio is ca 0.2. Finally, the recirculation rate, defining the cycling frequency, is also of importance.

(b)The variability of the results is larger than that observed in laboratory tests using collection strains of one given bacterium.

(c)Fecal coliforms can be removed totally in sunny days, after 4-6 h irradiation.

(d)Total coliforms and Ent. faecalis are largely removed, although in some experiments the count after 6 h irradiation time is not zero.

(e)Pseudomonas aeruginosa is apparently protected by the other strains, and/or by the starvation conditions of the experiments.

These conclusions lead to a positive evaluation of the feasibility to build larger reactors for water disinfection, but also indicate the need to solve the observed effect of bacterial consortiums.

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Synthesis and structure of bridged polysilsesquioxane xerogels functionalized by amine- and thiol- groups

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Bridged polysilsesquioxane (BPS) xerogels are a class of hybrid organicinorganic materials, formed by molecular building blocks. Such building units include a bridge of organic origin which links two or more Si atoms by forming hydrolytically stable Si-C bonds. BPS xerogels can be presented as bis(trialkoxysilanes) structures (RO)3Si-Rffi-Si(OR)3, where R is the methyl or ethyl radical, and Rffi denotes the organic bridge (spacer). By means of the appropriate precursors in the reaction of hydrolytic polycondensation it is possible to design on a molecular level the considered materials keeping control over their characteristics [1,2]Bridged polysilsesquioxane (BPS) xerogels containing amine (-NH2; -NH(CH2)2NH2; =NH)and thiol (-SH) groups were synthesized by hydrolytic polycondensation of 1,2-bis(triethoxysilyl)ethane, 1.4bis(triethoxysilyl)benzene and appropriate trifunctionalized silanes in the presence of a fluoride-ion catalyst in an ethanol solution. Obtained compounds have a porous structure (500-1000 m²/g) and a high content of functional groups (1-3 mmol/g). AFM data indicate that xerogels are formed by aggregating primary particles - the size of such aggregates is in the range 30-65 nm. It was established that the main factors influencing the structure and adsorption properties considered hybrid materials are: the nature and geometrical size of the functional groups, spacer flexibility and, in some cases, the ratio of the reacting alkoxysilanes and the ageing time of the gel [3]. Then, by fixing the aforementioned factors it is possible to control the texture of bridged polysilsesquioxanes with amine- and thiolgroups. Precise determination of these factors along with examination of the surface chemistry of xerogels obtained make it possible to create set of rules of desired synthesis of new hybrid organic-inorganic adsorbents. Particularly, by changing the nature and concentration of the functional groups on the surface it is possible to influence the interactions between adsorbate and adsorbent and tune the selectivity of functionalized BPS.

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Cyanide phytoremediation with water hyacinths (eichhornia crassipes)

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Cyanide is a highly toxic chemical, which has made it profitable to extract ore bodies containing only a few grams gold per ton. While most of the cyanide used in industrial mining is handled without observable devastating consequences, the not well regulated use and insufficient waste treatment in informal small scale mining suggest a novel economical cyanide waste treatment.

The water hyacinth Eichhornia crassipes may serve as an alternative for treating gold mining effluents because of its high biomass production, wide distribution and tolerance against cyanide and metals. We determined the phytotoxicity and elimination of sodium cyanide (NaCN) by E. crassipes. Toxicity was quantified by measuring the mean relative transpiration over 96h in a concentration range of 5-50 mg CN L-1. The EC50 value was calculated as 13 mg CN L-1 (probit analysis). Cvanide (5.8 & 10 mg CN L-1) was completely eliminated after 23-32 h (analyzed spectrophotometrically). Cyanide degradation was also measured in batch systems with leave and root cuttings, applying K14CN. After the experiments, about 40% of the radioactivity was found in the leaf-cuttings and 10% was converted to 14CO2 after 28 h, whereas the rootcuttings converted 25% into 14CO2 but only absorbed 12% in their tissues in 48 h. The Michaelis-Menten kinetics was determined with leave cuttings. The calculated half-saturation constant, KM, was 11 mg CN L-1, and the maximum metabolic capacity, vmax was 34 mg CN kg fresh weight -1 h -1. To evaluate the data in field scale, we performed cyanide degradation experiments over 2 months in a closed cycle treatment plant during the vegetation period of 2005. The installation was divided in a water hyacinth and a control channel with an open water surface. The dimensions of both channels were $0.68 \text{ m} \ge 6.5 \text{ m}$. We tested concentrations from 1-14 mg CN L-1. Free Cyanide (NaCN) was completely eliminated in a time frame of 24 h in the water hyacinth channel. The plants survived all treatments without observable toxicity symptoms.

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Coliphage virus removal from tertiary treated wastewater using Soil Aquifer Treatment System of Kwait

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Soil column experiments were carried out in order to assess the removal of viruses from tertiary treated wastewater by the Soil Aquifer Treatment (SAT) system in Kuwait. Tertiary treated wastewater was passed through soil columns filled with natural soil types. The types of soil that were used in column experiments included sandy soil from Sulaibiya area and calcareous sandy soil (locally named gatch). All columns were subjected to short flooding and drying cycles of one day each alternatively. Water samples were collected from the inlet and outlet of soil columns and analyzed for the concentration of coliphage virus. The concentration of coliphage viruses in the tertiary treated wastewater ranged between 300 and 62800 pfu/100 ml. The coliphage removal efficiency ranged between 78-100% for the gatch soil and between 58 and 100% for the Sulaibiya soil. The higher removal efficiency of the gatch soil could be attributed to its higher content of organics, carbonate and clays as compared to the Sulaibiya soil.

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Removal of heavy metal ions from water using raw and modified diatomite

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Heavy metal pollution in ecosystem is an important environmental problem encountered in many industrial areas. Lead, chromium, cadmium, copper, zinc, and mercury are among the most frequently observed metal contaminants. These metal ions are released to ecosystem at elevated concentrations as a result of unregulated application and inappropriate waste-disposal practices. Heavy metals are extremely toxic and threaten the living by joining the food chain. When they are released into the water, most of them are strongly retained and their adverse effects can last for a long time. Thus, it is important to apply an effective treatment method to wastewaters polluted with heavy metals. Heavy metals are generally removed from wastewaters by chemical precipitation, ion exchange, cementation, electrode position, membrane systems, and adsorption. In the last few decades, adsorption process has received much concern and has become an alternative to conventional precipitation technique, especially for wastewaters that contain low concentrations of metals and complex forming substances. Activated carbon is the most widely used adsorbent in the wastewater treatment. Owing to high cost of activated carbon, usage of the lowcost adsorbents such as agricultural wastes, metallurgical slags, fly ashes and various minerals have been investigated. In order to remove lead from aqueous solutions by using low cost materials such as iron oxides, francolite mineral, quartz and talk and bentonite, much work has been done However, no data has been reported for the adsorption of heavy metal ions onto diatomite or koeselguhrs. Starting from this point, in the present study, Pb2+, Cd2+, Zn2+, adsorption properties of natural diatomite of algerian origin and composite minerals (diatomite/charcoal) have been investigated. Langmuir and Freundlich adsorption isotherms have also been tested at various temperatures, and adsorption kinetic and some thermodynamic parameters have been determined.

This study showed that the mineral composites (diatomite/ diatomite) can be used as a new adsorbent capable to remove several toxic metals such as Pb(II), Cd(II), and Zn(II).

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Rheological study of Sol-Gel transitions in the thyxotropic systems: experimental study and computer simulation

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The rheological characteristics of the concentrated colloidal suspensions usually display a complex shear-rate-dependent behaviour. There are no reasonable explanation of the nature of viscosity growth at constant shear rate, of stressrate hysteresis, of non-stationary time dependence of viscosity and many other anomalous phenomena in complex thixotropic or rheopectic systems. This study involves both experimental investigation of the aqueous suspensions of the clay minerals with high solid phase levels close to those existing in benthals and other natural suspensions, used as constituents of medical compositions, and numerical simulation of rheological properties of the thixotropic suspensions. The numerical simulation model of the inhomogeneous network of inter-particles bonds, which accounts for both suspension destruction and suspension restoration abilities, is developed. It allows to simulate different inter-particles spatial distributions of the bonds. suspension destruction/restoration processes and time dependence of rheological behaviour.

The numerical simulation results are compared with the experimental rheological data for clay mineral suspensions with a distinct thixotropic effect. The anomalous thixotropic processes are shown to be related to a complicated structural self-organisation of the system at high shear rates, which is spatially inhomogeneous and involves formation of the local areas, characterised by the different strength of bonds. The system becomes spatially heterogeneous and divides into separate areas with the Newtonian and non-Newtonian fluidity. Such separation results in different shear rates and inhomogeneous flow velocity gradient. The numerical calculation evidences for heterogeneity existence at different spatial scales. A complex non-stationary behaviour of the effective viscosity and viscosity oscillations at large times of the rheological experiment were explained by the system self-organisation processes, developed at large time scale. The obtained results may be applied for explanation of other anomalies at the sol-gel transitions in a system with spatially developed coagulation bonds.

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Electrokinetic remediation of copper mine tailings

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The heavy metal contamination from mining industry has become a growing problem both in Chile and worldwide. This contamination includes large areas with soil pollution, contaminated rivers and continuous generation of mining waste deposits. The solid waste that will be analysed is mine tailings, which are the residual products after the flotation process in conventional sulfide copper mining. These tailings are known to contain considerable amounts of different heavy metals. Today the mine tailings are deposited directly on areas close to the mine without any controlled pretreatment or ground and surface water protection.

This work consists of series of electrochemical remediation experiments using an electric field as remediation agent in order to remove/concentrate heavy metals (specially copper) in a way that minimises the volume of contaminated matter significantly. During the experiments several parameters are monitored such as current density, voltage drop, pH in the soil/waste, metal mobility and removal rate. Adjustable parameters are current density, water content, distance between electrodes and remediation time. Furthermore, the remediation process can be optimised with the use of ion exchange membranes, which also is included in the experimental part of this project. Other parameters that will be discussed in this work are: the use of pulsed direct current, addition of dissolving or complexing agents, and use of different electrolyte solutions. It was found that electrochemical remediation of mine tailings and soil contaminated from mining industry could be an alternative to depositing the waste. To positive aspects are generated by this remediation technology: 1) an environmental friendly solid waste without elevated concentrations of metals, 2) a profit consisting of dissolved copper that can be used directly in the copper refinery proces meaning that natural copper containing minerals can be saved, and 3) a possible tool to recover copper from minerals with low grade.

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Biosorption of heavy metals in wastewater by the use of the algae Lessonia Nigrescens and Durvillaea Antarctica

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Copper smelting generates large amount of wastewater containing considerable amounts of inorganic compounds such as heavy metals and arsenic species. In order to maintain a high quality of fresh water resources these effuents have to be treated before the water can be returned to the ecosystems. Existing treatment methods such as sulfide or hydroxide precipitation create sludges that are difficult to handle. Furthermore, these methods consume considerable amounts of reagents in order to precipitate, coagulate and flocculate the contaminants. During the last decades the use of biosorbents has become interesting due to high adsorption capacities, low costs and regenerability of the sorbent.

The objective with this work was to test the sorption capacities and kinetics of arsenic (V) and different heavy metals such as Cu, Zn, Cd and Pb onto dried and size fractioned algae Lessonia Nigrescens and Durvillaea Antarctica. Both algaes are aboundant all along the coast of Chile. The results show that the biosortion is pH dependent with higher heavy metal adsorption at pH = 2.5. At pH 4.5 and 6.5 the adsorption was considerable lower. In general the adsorption of copper was promising good with Durvillaea Antarctica, and arsenic was sorbed better by Lessonia Nigrescens. During biosorption with both algaes the pH increased slightly in the wastewater indicating a complex ion-exchange/biosorption process.

The adsorption of the heavy metals seemed to follow both the Freundlich and Langmuir adsorption isoterms for the Lessonia Nigrescens but for Durvillaea Antarctica the Langmuir isoterm descibed better the adsorption equilibrium. The sorption kinetics of metals onto both algaecspecies could in general be explained satisfactorily by Lagergren's first order rate equation.

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Arsenic removal from copper smelter wastewater by electrocoagulation in an airlift reactor. Experiments and modelling

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Copper smelters - and the sulfuric acid plants that are connected to them generate large amount of wastewater containing heavy metals, where arsenic is the key contaminant. Heavy metals such as copper and lead can normally be removed by sulfide precipitation but arsenic needs other treatment.

Electrocoagulation to precipitate the arsenic through the in-situ production of ferric hydroxide was tested in an air lift reactor. This reactor was set up as two iron concentric cylinders. An airflow passing between the plates induced the mixing of the two phases - without the need of a stirrer -, generating turbulent conditions.

A set of synthetic wastewaters was used to test the performance of the reactor. The initial concentration varied from 100 to 5000 ppm of arsenic. Continuos current with current reversal each 120 seconds in order to avoid the passivation of the electrodes was applied. The gap between the electrodes was 10 mm for the reactor, and the current density was varied between 0.8 - 3 mA/dm2 depending on experiment. The reactor was run in continuos and batch wise operation, and the elapsed time for each experiment was 120 to 180 minutes. The results from the batch experiments were used to predict the performance of the continuos experiments and vice versa as a validation procedure.

In general the arsenic removal was efficient - e.g. a batch reactor experiment run at 1.2 mA/dm2 and initially 100 ppm arsenic showed that a more than 98 % reduction in the arsenic concentration after 3 hours was possible.

Residence time distribution experiments were run on both types of reactors, and a model that takes in account a) the kinetics on the solid phase (electrochemical phenomena), b) the mass transfer process, c) the ferrous ion oxidation with the ferric hydroxide production, and d) residence time distribution models, was developed and the kinetic parameters were fitted.

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Binary colloid systems of monodisperse SiO_2 sol-positively charged polystyrene latex as model system of polluted water purification

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The purification of water from fluidized colloid particles is an urgent task of the modern science. In order to simulate water purification the study of stability and heterocoagulation in binary colloid systems, consisting of monodisperse particles of SiO₂ sol (with isoelectric point in the range of pH=2) and positively charged particles of polystyrene latex in wide range of PH and indifferent electrolyte NaCl concentrations is done. It turned out that interaction in mixed system of polystyrene latex sol – SiO₂ sol highly depend on correlation of particle number of both components and pH of solution.

It is established, that the mixed systems with particles number ratio of 1:250; 1:500; 1:1000; 1:1500 and 1:2000 in the range of pH = 4-10 possess the aggregate stability close to stability of polystyrene latex. At pH=2 and pH=12 the obvious heterocoagulation in systems is observed.

At addition of indifferent electrolyte NaCl in systems with particles number ratio of 1:1000, 1:1500 and 1:2000 at transition from acid to alkaline environments the stability is considerably reduced, while for systems with particles number ratio of 1:250; 1:500 the values of coagulation limits are close to the coagulation limits for pure polystyrene latex and practically do not depend on pH.

The inference of interaction mechanism in mixed system is made, i.e. adsorption of highly dispersed component (SiO2) on globes of polystyrene latex, leading to charge exchange of their surface and to heterostabilization. Like charged mixture components are aggregative stable.

It is proved that using of modeling systems helps to scientifically solve different problems of polluted water purification.

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Evaluation of an integrated low tech bio-coagulant-sand

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One of the recent innovations in household water and waste water treatment is the biosand filter which allows users to obtain treated water on an intermittent basis while taking full advantage of the reliability and effectiveness of slow sand filtration. Despite the comparatively better water treatment potentials of the biosand filter, it cannot purify very dirty and turbid water (the kind of water samples gotten from the ponds in the study area) at one stretch. It is in this view that the need arose to evaluate the potentials of an integrated low tech bio-coagulant-sand filter using bacterial culture tests, total solids, and turbidity.

In this study, hundred liters of three surface water samples each was pre-treated with pasted 60 seeds of Moringa and further filtered through a concrete biosand filter made from locally available materials, concrete, sand, gravel and pipe. The mean total aerobic mesophilic bacterial counts, coliform, E coli, pseudomonas, yeast counts, as well as turbidity of the untreated water drastically reduced to WHO acceptable standards for potable water. Results also showed that the mean values of the same parameters from biosand filtered water alone were significantly lower than the corresponding mean values obtained for Moringa treated water. This however indicates that biosand filters are more efficiency in purifying water than the seed powder of moringa oleifera.

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Intensification of electrokinetic remediation of metal-contaminated soil

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Electroremediation of industrial contaminated soils from heavy metals is a very important and complicated problem. The method is based on a mass transfer of polluting substances under action of an external electrical field with their subsequent extraction from a cathode chamber. Transfer of components of soil occurs by electrophoresis, electro-osmosis and diffusion and depends on different accompanied factors.

Most important and effective process that causes the electrokinetic purification of soil from charged pollutants is electrophoresis. To provide the mobility of pollutants in an electric field, they should be not only desorbed from complexes with soil components, but also during the whole process of soil remediation should preserve their water-soluble form. However, due to a generation of hydroxyl ions on a cathode and, correspondingly, by an alkalinity of water in the cathode chamber and in the soil adjacent to it, the considerably part of metallic pollutants loses their solubility and therefore decreases or loses their mobility in an electric field. Therefore the careful optimization of the known methods of pH regulation or the development of new ways of pH regulation is one of the most important problem of soil remediation that worthy of special attention.

The conducted theoretical analysis of all processes during soil remediation and experimental investigations gave an opportunity to develop an original scheme of pH regulation, which allowed us to accelerate and to enhance the soil decontamination. The received experimental data concerning the purification of a sod-podzol soil, polluted with nickel and cadmium compounds, have shown that the high degree of remediation (more than 99%) during relatively short treatment is reached.

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Biocolloid methods to remove heavy metals and radionuclides

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The heavy metal contamination of environment which is one of the most dangerous type of contamination has stimulated the search of new soft technologies to remove these pollutants.Biocolloid methods to remove heavy metals and radionuclides which include biosortpion and bioaccumulation are the most ecologically appropriate techniques. Biosorption is a term describing removal of heavy metals and radionuclides via the passive binding to dead biomass from aqueous solution. This implies that the removal mechanism is not controlled metabolically. In contrast, the term bioaccumulation describes an active process, whereby removal of metals requires the metabolic activity of living organism.

Because bacterial walls are complex in their composition, the key mechanism of metal ion removal consists in formation complexes among them and functional groups available on surface.

Investigations of microbial biosorption of metals to remove heavy metals and radionuclides to rate the adsorption or complexation of them (e.g., uranium, strontium, cesium) by biomass from mine and other wastewater were made. The main characteristics of this process nere determined, it was shown that the maximum uranium sorption by both *Bacillus polymyxa IMV 8910* culture and the natural association of the active sludge organisms we have shown is observed within the pH range 4–6.

In fact, most microbial surfaces are negatively charged because of the ionization of functional groups, thus contributing to the metal binding. The high adsorption of the biomass within some pH range might be explained by the fact that biosorption of metal ions on living biomass is due to surface binding followed by intracellular uptake. The biosorption of metal ions on dead biomass is accomplished via only surface and wall binding, which is non-metabolic. At kinetic trials, adsorption of such a great cation as uranyl by the living organisms of active sludge and *B. polymyxa IMV 8910* cells is higher than that by the dead ones.

The experimental results reached can be interpreted through a detailed analysis of the surface properties of microorganism cells where one can select two layers forming properly the dense part of double electrical layer. The first layer is the outer membrane, a structured layer depending on the cell type consisting from proteins, lipids, etc. The second layer is the capsule of a polysaccharide or polypeptide nature or a hydrophilic slime. The diffusive ionic atmosphere consisting around a cell compensates the charge of ionogenic groups consisting both in the first layer and second one. The biosorption process may occur in both the first and second layers varying both charge and structure of the double electrical layer existing hitherto. The mechanism of biosorption process based on surface complexation model was proposed. The triple layer model was used to quantify the adsorption data.

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Polysaccharide-induced flocculation of colloidal clay. Roles of pH, valence and concentration of counterions, and macromolecule structure

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It is widely recognized that organo-mineral interactions have a great importance in environmental processes by forming aggregates. Such aggregates increase mechanical cohesion in soils on one hand, and on the other hand influence the transfer of particulate matter and associated pollutants and nutriments in runoff waters and rivers by controlling the colloidal stability of suspended matter. The present work is focused on the aggregative interactions between the two main reactive organic and mineral constituents in soil, that are microbial polysaccharides and swelling clays. А succinoglycan (weakly acid polysaccharide) and a diluted Na-montmorillonite suspension were used. The colloidal stability of the clay suspension in the complex system "water/clay/salt/polysaccharide" was studied as a function of the ionic strength and succinoglycan concentration.

Adsorption isotherm revealed that adsorption of polysaccharide onto montmorillonite particles requires prior screening of the interparticular electrostatic repulsions by the addition of a coagulating salt in a concentration at least equal to the critical coagulation concentration measured in a "water/clay/salt" system. Size measurements by laser diffraction showed that such adsorption induces bridging flocculation of the suspension with an optimal polysaccharide/clay weight ratio around 2 %. Moreover, varying the nature of the salt used (CaCl2, NaCl) revealed that the valence of the salt had no effect on the polysaccharide-induced flocculation, and thus that polysaccharide are not linked to clay via divalent Ca2+. Instead of this, varying the pH of the suspension allowed to propose that clay - polysaccharide interactions occur between acidic groups of the macromolecule and positively charged edges of clay sheets at acidic pH.

Moreover, by using different kinds of bacterial polysaccharides (succinoglycan, xanthan, gellan, dextran), we could vary the physical and chemical properties of the macromolecules, like density and localisation of charge, spatial conformation, and size. It appeared that polysaccharide-clay interactions are much favoured when macromolecule acidic groups are localised on the side-chains, well exposed toward the outermost, improving the efficiency of sticking when colliding with neighbour clay sheets.

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Removal of chlorinated phenols from wastewater by free and immobilized laccase from roots of *Chenopodium album*

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Enzymatic treatmant is currently considered an alternative method for the removal of toxic xenobiotics from the environment and has attracted much interest recently. The theroy of enzymatic treatment is that carcinogenic chemicals such as phenols are polymerized forming new substances which are less water soluble and then the precipitate is separated from water by filtration. Thus, this work focuses on the development and evaluation of a process for the removal of chlorophenol from wastewater using free and immobilized laccase. Laccase (Ec 1.10.3.2) used in this application was isolated from the root of Chenopodium album a wild plant in Egypt and immobilized in a system of chitosan and alginate. The immobilization matrix consisted of a chitosan matrix cross-linked with glutaraldehyde with an alginate-filled pore space. 2.4-Dichlorophenol was quickly and completely transformed throughout 20 h than 4-chlorophenol by the effect of 5 units ml⁻¹ of laccase. The transformation process of either 4-chlorophenol or 2.4-chlorophenol by immobilized laccase was more effective than by free enzyme. Increasing of laccase concentration from 10 to 50 units ml⁻¹ resulted in corresponding increase in the transformation of both 4-dichlorophenol and 2,4-dichlorophenol. Adding 2,4-dichlorophenol to 4chlorophenol at various initial concentrations throughout 20 h, resulted in reducing the transformation of 4-chlorophenol by increasing 2,4-dichlorophenol concentration. Similarly, 4-chlorophenol inhibited the transformation of 2,4dichlorophenol at all concentrations investigated. These results in this work reveal that oxidoreductive enzyme such as laccase could oxidize a mixture of chlorinated phenols. The use of laccase for the bioremediation of complex wastewater appears promising.

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Structure forming in erosion soil by water soluble polyelectrolyte and their interpolymer complexes

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The water-soluble polymers (WSP) and their interpolymer complexes (IPC) are widely used to control of the surface phenomena in disperse systems, in particular, in the mineral dispersions. The main importance of utilization of WSP and IPC can be connected with the possibilities of controlling their conformational, electrochemical and surface-active properties.

In this work the data of investigation of colloidal - chemical properties polydimethyldiallylammonium chloric (PDMDAAC), polyethyleneimine (PEI) and their interpolymer's complexes with some carboxylated polymers are stated: unufloc (UF), sodium of carboxyl methyl cellulose (Na-CMC) and methyl cellulose (MC) with the purpose of constructing a new structure forming and fixing agents of surface layer of soils were reported.

With the deterioration of an ecological condition of a surface, formation of radioactive spots on soil, erosion of virgin lands, etc. the problem of restoration of structure and clearing of the soil arises. The decision of these problems can be achieved by regulation of structural - mechanical properties of soils by means of the water-soluble polymers. In this case it is possible to form surface film which possesses high resistant to wind and water erosion and reduces mobility of the soil particles containing radioactive nuclides and heavy metals.

For the first time on the basis of the modern theory of resistance of lyophobic sols DLFO the interaction energy of particles of soil in conditions of perikinetic and orthokinetic coagulation in dependence on particle sizes and pH suspensions was calculated. It was established that under interaction of the smallest particles (a = 1 micron) the perikinetic coagulation started at value of pH ≤ 5 . The perikinetic coagulation of large particles (a = 12 micron) corresponds to the range of pH ≤ 4 while the mixtures of particles of soil with various diameters ($a_1 = 33$ microns and $a_2 = 2$ microns) orthokinetic coagulate at pH ≤ 5 being defined by behaviour of the smallest particles.

The interaction of oppositely charged polyelectrolytes (Na-CMC, MC and UF with PDMDAACh and PEI) in an aqueous medium was investigated by means of viscosimetry, spectophotometery and macroelectrophoresis methods. It was found that interaction of the above mentioned polyelectrolytes is accompanied by essential decreasing of reduced viscosity (up to 0,1-0,15 dl/g, that is typical for condensed macromolecules of globular proteins) and increasing of turbidity as well as the inversion of electrokinetic (ζ) potential takes place. The obtained data evidence for formation of interpolymer complexes between anionic and cationic polyelectrolytes in the soil volume.

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Complexation of betainic hydrogels with ionic surfactants

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The interaction of betainic hydrogels with cationic (cetylpiridinium chloride (CPC)) and anionic (sodium octylsulphonate, sodium dodecylbenzosulphonate) surfactants in an aqueous solution was investigated. Betainic gels were synthesized by means of end cross-linking method of alkylated by monochlor acetic acid polyethylenimine (PEI-alc) with epichlorohydrin. The increase of the alkylation degree of PEI (β) results in significant propagation of swelling coefficient (K_{\star}) of the betainic hydrogels that can be explained in accordance to the repulsion between quaternized nitrogen atoms and also by contribution of their counter-ions to the osmotic pressure of the networks. The addition of detergents to the solutions in which hydrogels were swollen causes their contraction. The amplitude of compression of the networks increase with increasing of alkylation degree of macromolecular chains of PEI-alc between cross-linking points. Contraction of the networks is explained in terms of formation of polyelectrolyte complexes in the bulk of hydrogel due to electrostatic contacts between quaternized and protonized nitrogen atoms of betainic gels and sulphonic groups of anionic detergents. The hydrogel - cationic detergents complexes is formed due to the electrostatic contacts between carboxylic ions of betainic networks and pyridinii ions of CPC. The complexes are also stabilized by hydrophobic interactions between non-polar parts of hydrogels and surfactants respectively. It has been shown that at small concentration of surfactants their penetration into the gel volume is complicated because of unbalance of electric potentials of hydrogel surface and detergent ions. The surfactant ions render strong influence on conformational state of macromolecules between cross-linking points of the networks. It was found that there is a displacement of an isoelectric point of hydrogels in the presence of surfactant molecules. Anionic sufactants result in disappearance of left part whereas cationic surfactants - right part of the dependence of K_e on pH medium. It is necessary to note that the similar behaviour is characteristic for amphoteric macromolecules in which oppositely charged functional groups are situated in different monomer units.

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Complexes of vinyl lactam based hydrogels with phenol molecules and surfactant ions

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The interaction between poly(N-vinylcaprolactam) (PVCL) and its copolymer with sodium itaconate (PVCL-ITNa) hydrogels and phenol molecules has been investigated. It was found that the addition of phenol to non-charged hydrogel results in its contraction whereas picric acid (PA) causes collapse in both neutral and charged networks. The driving force of complexation of PVCL gel with phenol molecules seems to be H-bonds arising from interaction of carbonyl group of the lactam cycle and hydroxylic groups of phenol through of water molecules. For the GPVCL-PA system is possible also to allow the similar mechanism. The adding reason of collapse of the neutral network at complexation with PA can be occurred by ion pair formation between functional groups of the gel and picric acid.

This conclusion was made on the basis of comparison of ionization constants of phenol and PA (K_a^{Ph} =1,3^{10¹⁰} and K_a^{PA} =1,6^{10⁻¹}). Due to high acidity the proton of hydroxyl group of PA is movable and capable easily to bind to electron-donating oxygen atom of carbonyl group of lactam cycle of PVCL network. This results in redistribution of electronic density in a benzene ring and signify that the nitrogen atom of amide group acquires positive charge. The mole ratio [Ph (PA)]/[gel] at which collapse takes place shifts to smaller value with increasing both of concentration of charged groups of networks and acidity of organic components. For removing of sorbed molecules of phenol and picric acid the swelling coefficients of dried complexes with their pure gels in various solutions of electrolytes were studied. We have found that with increasing of concentration sodium hydroxide up to 0,1 M all previously sorbed phenol and picric acid molecules desorbes again in the surrounding gel solution. Obtained data should be used to utilize for the decision the problems of purification of waste water from the high contents of phenol and its derivatives.

The shear modulus of (G_n) of polyvinylpirrolidone gel (PVPD) depend on the concentration of sodium dodecylbenzosulphonate (SDBS) in an external solution was studied. It was obtained that in a concentration interval of SDBS running from 0 up to 10^3 M both volume and shear modulus of a neutral network practically are not changed. However at [SDBS]> 10^3 M the significant growth of volume and shear modulus of the hydrogels takes place that would be explained by intensive penetration of surfactant ions in the volume of PVPD gels, which counter-ions create a high osmotic pressure. It appears feasible to assume that the concentration of surfactant when the growth of volume of the neutral networks takes place corresponds to the first critical aggregation concentration (CAC-1) of detergent, which as a rule does not depend on a volume fraction of polymer in the swollen gel. The second critical aggregation concentration (CAC-2) or critical micellation concentration (CMC) of surfactant ions corresponds to a maximum on logQ-IogC_{SDBS} dependence.

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Rendering of ions of toxic metals on the basis of polymeric compositions

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The large attention is given to reception and research of properties of polymeric complexes on the basis of polyelectrolytes and of low molecular ligands on the part of the chemists of different scientific schools. These investigations are devoted not only study of properties and structure of polyelectrolyte complexes (PEC), but also have significant results on their practical application in various areas of science and engineering: as polymeric compositions for clearing water from micro- and macrocolloids, implantations of various organs, sorbents of ions of metals, matrixes for immobilization of ferments etc.

In the given message the results of investigations of interaction processes of polyethyleneimine (PEI) with various of polydentatic lowmolecular ligands are resulted. Polyethylenimine carries out a role of a polymeric matrix, and lowmolecular ligands, fixed on a surface of PEI is sources of functional groups for concentrating of ions of metals.

The results of physico-chemical investigation of these processes by various methods: potenciometry, conductimetry, viscosymetry, IR spectroscopy have allowed to establish schemes of interphase interaction of components, compound, structure and properties of received polymeric complexes. The conditions of reception of polymeric compositions on the basis of PEI, 2,3-dimercaptopropansulphonatic of sodium (unithiol) and sulfosalicilic acid were developed which was successful is used for rendering of ions of mercury (II), beryllium (II), chromium (concentrating III), chromium (VI), lead (II), and also for extraction of ions of gold (III) and silver (I) from solutions of industrial sewage water.

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Physical and mathematical modelling of the processes of radio-active contaminants transfer

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After Chernobyl atomic power station accident the most widespread and the most dangerous radionuclides on contaminated territories of Ukraine are considered the elements to be as follows: Cs¹³⁷, Sr⁹⁰, Pu²³⁹ and Am²⁴¹. Migration of radionuclides which are fallen into the soil leads to its vertical and horizontal redistribution in consequence of which the radionuclides are getting into subsoil waters, reservoirs and plants. It is known that peculiarities of spatial redistribution of radionuclides to a considerable extent depend on physical and chemical condition in which particles are being and also on processes of its local transformation. Description and prognosis of radionuclides migration in geological structures which are based on definite physical and mathematical models which identically take into consideration physical and chemical peculiarities of radionuclides, geochemical characteristics of soils and weatherclimatic conditions. According to the previous researches in soil mass it has been isolated location of radionuclides in following forms of fuel particles: watersoluble, exchange-sorbate, acid-soluble and fixed and also various schemes of its transportation have been worked out. In the research each scheme of transformation and migration of radionuclides in the soil has been corresponded to definite mathematical model. The purpose of this research is to conduct the analysis of models of vertical radionuclides transfer in water saturated porous isotropic environments (soils) under condition of movement absence of pore solution. Analysis of the received results of experimental research shows that principal amount of Cs^{137} , Pu^{239} and Am^{241} particles are being in nonexchangeable form in all soil types whereas principal amount of Sr⁹⁰ particles are divided between exchangeable and non-exchangeable forms. Therefore the researches of transfer of Cs¹³⁷, Pu²³⁹ and Am²⁴¹ particles are to be conducted on the basis of models in which it has taken into consideration the possibility of particles being in trapping sites. It has also been revealed that Sr⁹⁰ particles migration is to be described by models without taking into consideration fixation of the additions. The mathematical calculations have showed that presence of particle trapping sites assists radionuclides accumulation in the soil. It has been revealed that significant effect on profiles of contamination concentration and summary flows of the additions has a coefficient of surface distribution of addition substance between water pore solution and adsorbed layer of water. Coefficients of diffusion and intensity of sorbing and desorbing processes influence on concentration and flows values but do not change its qualitative behaviour.

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The mechanical mixing for intensifying the direct multi-stage filtration process

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At present, it is a very urgent task to intensify the direct multi-stage filtration process and to improve economical characteristics of water treatment and sewage purification plants as well as to obtain the high quality of filtrate. Technology of the direct multistage filtration is realized through several rapid granular filters that are connected in series. It has the main advantage: the possibility for intensifying the filtration process before the every filter stage. It can be realized through optimal reagent (coagulants, flocculants) treatment, and the usage of the new highly effective granular materials, the modification of their surfaces, as well as using special types of physical enhancement, for example, the mechanical mixing of the suspension. As the structure of sediment in filter porous media, its degree of hydrated, density and firmness to the hydraulic impact of the water flow defines the attachment–detachment particle processes during filtration.

In our experiments we use blade mixer with such velocities from 60 up to 240 rotations per minute, so the average mixing velocity in reaction camera is from 0.2 up to 0.8 m/s. The time of mixing is 5–8 minutes. The modeling suspension is treated by coagulant (Dopt=10 mg/dm³ of aluminum sulfate) and then filtrates through the filter of the first stage with the constant velocity 10 m/h. On each stage we use the similar filter granular of quarts sand with diameter 1.0-1.25 mm, the thickness of the layer is 50 mm. The first stage is operated behind its protective granular duration, so the quality of its filtrate is getting worse in time. The filtrate is collected in reaction camera where it is mixed and than flows through the second stage of the filter. Filtrate of the second stage with mixing (or without it) flows through the third filter stage.

The best results have been obtained under the mixing velocity 200–240 rot/min, which provide condensation of the most diffused parts of the flocks. The usage of mixing before the second stage gives possibility to intensify the operation not only for the second filter, but for the next (the third) one too. Analysis of the curves for granular head losses in the second and the third stages show the decreasing of these parameters in 1.75–2.0 times. The summary head losses (in three stages) diminish in 1.5 times. So the duration of filters operation to get the maximum limited values of the head losses can be increased sufficiently. The quality of the treated water is up 20–45 % higher.

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