Polymer-Supported Iron Nanoparticles and Microparticles as Remediants for Subsurface Contaminants

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Soil and groundwater contain a legacy of chemical substances - including halogenated organics and toxic metal ions - from industrial and agricultural processes. A decade ago, scientists at the University of Waterloo developed a remediation method based on zero-valent iron, which has since been investigated by numerous researchers. Chemical reduction by iron converts halogen-containing compounds to relatively innocuous hydrocarbons, and reducible metal ions (Cr(VI), Pb(II), Hg(II), As(V), Tc(VII)) to less soluble forms. Still, the inaccessibility of the deep subsurface and the large volume of soil or water affected by a chemical spill make the clean up of contaminants both costly and technically daunting. To address this problem, we have developed anionic polymers and sulfonated carbons as "delivery vehicles" to transport metal particles through soils. These polyelectrolyte supports prevent particle aggregation and lower the sticking coefficient of iron particles in saturated sand and clay soils to ca. 0.01. We find, in good agreement with theory, that submicron particles have the most favorable transport characteristics. Field tests show facile injection of iron particle slurries at depths up to 10 meters and reaction with subsurface chlorinated organic compounds on a timescale of days to weeks.

Targeted Delivery of Nanoiron to the NAPL-water Interface

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NAPL source area remediation can decrease mass flux from the site and can expedite remediation. Nanoiron can rapidly degrade NAPL (e.g. TCE) to non-toxic products in situ, but methods to deliver it to the NAPL-water interface are needed for efficient use of the iron. Delivery requires the ability to transport through water-saturated porous media without being filtered out, and the ability to locate the iron at the NAPL-water interface where it can degrade NAPL. The approach developed to provide surface functionality to the nanoiron is similar to targeted drug delivery and may be used to target other specific locations in the subsurface. We demonstrate here the ability to functionalize the reactive nanoiron particle surface for providing efficient transport through the subsurface and preferential partitioning to the NAPL-water interface. Surface modification by amphiphilic block copolymers with highly controllable properties was used to manipulate the electrostatic repulsive forces of the nanoiron, and to increase the iron’s affinity for the NAPL/water interface. The results presented here will show the success of the surface modification in terms of transportability and targeting. Transport of the nanoiron modified by commercially available conventional surfactants and block co-polymers was also examined, and results are presented to demonstrate the relative effectiveness of the synthesized polymer compared to the other modifications. Emulsification of trichloroethylene
using synthesized polymer modified particles will demonstrate the ability of the particles to localize at NAPL-water interface.

8-3

Synthesis of Magnetite Nanoparticles from Reclaimed Acid Mine Drainage
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The synthesis of magnetite nanoparticles has been the focus of numerous recent research efforts. In each case, magnetite nanoparticles were formed from reagent-grade chemicals. It is known that acid mine drainage (AMD) produced through coal mining in the Mid Appalachian region can produce waters low in pH and high in dissolved metals, of which iron is most abundant. In this study, Fe was recovered as a ferric hydroxide solid from an AMD water collected from an abandoned coal mine. After solid-liquid separation, the AMD was neutralized to remove other dissolved metals. The resulting supernatant met National Pollutant Discharge Elimination System (NPDES) requirements for discharge. The Fe precipitate was the resolublized and used for magnetite nanoparticle synthesis via coprecipitation at room temperature under nitrogen atmosphere. Based on transmission electron microscope (TEM) and scanning electron microscopy (SEM) observations, most of the magnetite particles ranged from 10 to 15 nm and were spheroidal in shape. Thus, the synthesis of magnetite nanoparticles with the iron recovered from AMD was feasible. Consequently, it is possible to address the need for raw feed stocks in nanoparticle manufacturing, while simultaneously reducing AMD sludge disposal liabilities.

8-4

Bridging the Gap between Macroscopic and Spectroscopic Studies of Metal Ion Sorption at the Oxide/Water Interface
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Metal sorption mechanisms were investigated for strontium, cobalt, and lead sorption onto quartz and gibbsite using sodium chloride, nitrate, or perchlorate as background electrolytes. Spectroscopic analyses of concentrated sorption samples were evaluated for their ability to provide insight into the controlling sorption process for more dilute systems. For strontium, outer-sphere complexes identified using x-ray absorption spectroscopy (XAS) of concentrated samples were consistent with macroscopic sorption data collected in more dilute systems. XAS results indicated that cobalt formed new solid phases with dissolved silica or aluminum on oxide surfaces. Macroscopic experiments of cobalt sorption supported the spectroscopic data for total cobalt concentrations of 10^{-5} M. At lower total cobalt concentrations, adsorption appeared to be the prevailing mechanism of cobalt removal. Spectroscopic and macroscopic results suggested that lead adsorbed as an inner-sphere complex on oxides and that the presence of chloride affected the extent of sorption, respectively. This result was attributed to competition with aqueous lead-chloride complexes based on thermodynamic calculations. The overriding theme of the analysis of these data is that neither spectroscopic analysis nor trends in macroscopic data alone can completely explain the sorption behavior observed in oxide/water systems. The
extrapolation of conclusions drawn from data collected at relatively high surface concentrations to more dilute systems must be analyzed in conjunction with aqueous phase thermodynamic data.

8-5
Surface Characterization of a Novel Material for Arsenic Removal
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A selective sorption material composed of iron hydroxide and activated alumina, designated iron-enhanced activated alumina (IEAA) has proven to successfully remove arsenic to below the MCL of 10 ppb. In contrast to many other materials developed for the same purpose, IEAA has the ability to remove both ionic forms of arsenic, (As(III) and As(V)). While the mechanism for removal of As(V) may be trivial, that for the removal of As(III) is unknown and requires study. Extended X-ray Absorption Fine Structures (EXAFS) and X-ray Near Edge Spectroscopy (XANES) have been used for surface characterization of this material in the presence of As(III). Results from these studies will provide detailed information concerning the coordination environment of the adsorbed arsenic species on the surface of the IEAA. From this we will can develop a better understanding of the mechanism for removal of As(III), and hence move to a more efficient design and synthesis of this IEAA. We will present data from column experiments demonstrating the efficient removal of As(III) as well as the results from spectroscopic studies of this material loaded with different forms of Arsenic.

8-6
Novel Nanostructured Anatase Assemblies from Algae as Strong Catalysts for the Hydrolysis of Organophosphorous Esters
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Novel nanocrystalline anatase (TiO₂) assemblies were produced from biologically self-assembled SiO₂-based diatom microshells (frustules) via a unique reactive conversion technique. This conversion involves a halide gas (TiF₄)/solid displacement reaction that allows for the complete conversion of SiO₂ to TiO₂ while preserving the starting bioclastic structure. The resulting nanostructured anatase frustules were found to strongly catalyze the hydrolysis of methyl paraoxon and methyl parathion under mild conditions (pH 4.5-9, 25° C), with catalytic effects of 5-25 times greater than that of other commercial anatase nanoparticles. Characterization of these anatase nanomaterials revealed isoelectric points in the range of 2.5 to 4.5, which were lower than for typical anatase (pHIEP of 5.2-6.0), indicating stronger surface acidity. Quantitative fluorine analysis after the conversion reaction indicated that the amount of residual fluorine in the nanocrystalline anatase played a significant role in the surface acidity and in the catalytic effect on the hydrolysis of the two organophosphorous esters.
Comparison of Surface Complexation Models for Predicting Bi-Solute Metal Ion Sorption onto Iron Oxides

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Surface Complexation Models (SCMs) hold significant promise as a tool for predicting the fate and transport of metal ion contaminants. The reliability of SCMs is dependent on the selection of appropriate surface complexation reactions and accurate estimation of the model parameters. The past decade has seen significant improvements in model reliability due to increased use of spectroscopic data for guiding the selection of surface reactions. Yet, many of the intrinsic SCM parameters are correlated with each other and a wide range of parameter sets can still be used to fit single-solute adsorption data equally well. One parameter that contributes to data uncertainty and is required in all SCMs is the surface site density of the adsorbent that is often determined by fitting experimental data. The estimation of the surface site density using an independent technique can limit the resulting set of parameters that fit the adsorption data. In our research, we have shown that site densities estimated using the tritium exchange technique provide better triple layer model SCM predictions of bi-solute metal ion sorption. In this paper, we extend this work to provide a comparison of two SCMs, the diffuse layer model and the triple layer model, for predicting competition of metal ion sorption onto iron oxides over a wide range of experimental conditions that include adsorption and surface precipitation as the predominant sorption process.

Mechanisms Controlling the Release of Trace Elements from Clean-Coal Technology By-product: Effect of Proton and Organic Ligands

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Despite numerous studies aimed at increasing the utilization of fixed flue gas desulfurization (FGD) by-products, concern about the leaching of hazardous constituents has limited the beneficial re-use of these materials. Furthermore, there is a lack of understanding regarding kinetic processes that control the leaching of trace elements. In this study, the release of trace elements from fixed FGD material was investigated by considering bulk diffusion, pore diffusion, and surface chemical reactions as possible rate controlling steps. A flow-through rotating disk system and shrinking core model (SCM) were used to determine the rate-limiting process. Experimental results and modeling indicated that the leaching process was controlled by surface chemical reactions. As a result, the leaching rate can be described by a combination of an intrinsic hydration reaction and a proton-promoted dissolution reaction. The effects of organic ligands, i.e., citric acid, oxalic acid, and humic acid, on leaching kinetics were also investigated under both acidic and near neutral conditions. A ligand-promoted effect was only observed with citric acid. In the case of oxalic acid, formation of calcium oxalate on the surface significantly inhibited the leaching process. The adsorption of humic acid selectively inhibited the leaching of Fe with no significant effect on the leaching of other elements.
Absorption and Adsorption of Hydrophobic Organic Contaminants to Black Carbon Soots
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Single solute sorption isotherms from aqueous solution were obtained for diesel soots and hexane soots using phenanthrene and 1,2,4-trichlorobenzene as sorbates. Substantial isotherm nonlinearity was observed in all cases. Compared to sorption with diesel soot SRM 2975, sorption with diesel soot SRM 1650b was lower at low concentrations but higher at high concentrations. Pore size distribution and BET surface area (BETSA) were calculated using nitrogen adsorption data. Comparison between pore size distribution-normalized and BETSA-normalized uptakes for the studied sorbents and those for activated carbon was used to show the relative importance of surface adsorption to overall uptake. Adsorption dominates for three soots (SRM 2975, hexane soot, and oxidized hexane soot) at all concentrations and for the fourth soot (SRM 1650b) only at low concentrations. For SRM 1650b, a dual domain model is required for description of the total sorption isotherm of both sorbates studied, with absorption dominating uptake at higher sorbate concentrations.

8-10
Colloids Partitioning between Organic and Aqueous Phase Cause the Low Interfacial Tension of DNAPL
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Many low Interfacial tensions (IFT) have been observed between some field Dense Non-aqueous phase liquid (DNAPL) and water comparing to the original organic compounds. But little study has been done to study the mechanisms lower the IFTs. A DNAPL sample recovered from Savannah River Site (SRS) of Department of Energy (DOE) also showed an extreme low interfacial tension (IFT), which is less than 2 Dynes/cm. The main composition of the DNAPL was analyzed to be about 80% PCE and 20% TCE, which have IFTs of about 45 Dynes/cm and 35 Dynes/cm respectively. When we equilibrated the DNAPL with water, white fine precipitates are observed to accumulate on the interface. And the further study of the IFT between the SRS DNAPL and water over time using a picture pendent drop goinometer showed that the precipitates could account for the substantially lower IFT. The formation of the precipitates can be reasoned by the partitioning of the co-disposed chemicals accumulating on the interface when the DNAPL contacts aqueous phase. Research works has been done with a chelating agent EDTA and tin, which was analyzed to be present in DNAPL to examine the influence of its presence on the IFT. While no evidence showed that the tin itself can account for the substantial low IFT of SRS DNAPL.

8-11
Application of ac Electrokinetics in Membrane Filtration Processes
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A novel combination of ac dielectrophoresis with crossflow membrane filtration is proposed for separation of the components of aqueous and non-aqueous colloidal systems. The dielectrophoretic forces experienced by a colloidal entity can be attractive or repulsive depending on the dielectric properties of the solvent and the dispersed phases and the frequency of the applied ac signal. Embedding an array of electrodes on a semi-permeable membrane and actuating them with an appropriate ac signal allows manipulation and separation of the constituents of a colloidal suspension or microemulsion. The attractive forces can be employed to preferentially separate the dispersed phase in an emulsion. In contrast, the repulsive dielectrophoretic forces can be utilized to prevent deposition of colloidal particles on the membrane. An analysis of the pertinent transport processes during dielectrophoretic membrane filtration is presented. The simulation results from the trajectory analysis of particles in presence of dielectrophoretic and hydrodynamic forces indicate: (a) attractive dielectrophoretic forces can result in a significant enhancement in the transport of the dispersed phase toward the membrane and (b) repulsive dielectrophoretic forces can prevent colloid deposition onto the membrane and, hence, membrane fouling, in an entirely physical manner.

Monte Carlo Simulation of Colloidal Membrane Filtration: Principal Issues for Modeling
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The principal issues involved in developing a Monte Carlo simulation model of colloidal membrane filtration are investigated in this study. An important object for modeling is the physical dynamics responsible for causing particle deposition and accumulation when encountering an open system with continuous outflow. A periodic boundary condition offers a solution to the problem by re-circulating continuous flow back through the system. Scaling to full physical dimensions will allow for release of the model from flawed assumptions such as constant cake layer volume fraction and thickness throughout the system. Furthermore, rigorous modeling on a precise scale extends the model to account for random particle collisions with acute accuracy. A major finding of this study proves that forces within the colloidal filtration system are summed and transferred cumulatively through the inter-particle interactions. The force summation and transfer phenomenon only realizes its true value when the model is scaled to full dimensions. The overall strategy for model development, therefore, entails three stages, first, rigorous modeling on a microscopic scale, next, comprehensive inclusion of relevant physical dynamics, and finally scaling to full physical dimensions.

Humic Acid Removal with Aminated PGMA Beads
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Humic substances are ubiquitous in natural waters and can cause various environmental and potential health problems. Adsorption has been one of the methods to minimize the presence of
humic substances in water supply. In this study, novel PGMA (poly-glycidyl methacrylate) beads were prepared and aminated with ethylenediamine (EDA) as an adsorbent to remove humic acid from aqueous solutions. Zeta-potential analysis was conducted to examine the surface electrostatic properties, and atomic force microscope (AFM) was used to examine the surface morphologies of the adsorbent (PGMA-EDA) with and without humic acid adsorption. Fourier transform infrared spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) were utilized to reveal the surface interactions in humic acid adsorption. It was found that the PGMA-EDA adsorbent is very effective in humic acid adsorption and the amine groups play an important role in interacting with humic acid to be adsorbed. Model fitting study showed that the adsorption follows a pseudo-second-order (PSO) kinetics.

8-14
**Colloids in Subsurface Environments: Aggregation, Deposition, and Facilitated Transport.**
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Many transport processes in natural aqueous environments are dictated by colloids and their interactions. Prominent examples include formation of a river delta or colloid facilitated transport of contaminants in the subsurface. Mutual interaction between particles and surfaces bear many similarities. For example, homoaggregation processes between identical particles are of relevance in ripening or pore clogging phenomena, while heteroaggregation processes between unequal particles bear close analogies to particle deposition. The lecture will discuss several recent techniques and developments allowing us to study such aggregation and deposition processes experimentally, and the possibility to quantify those processes with the theory of Derjaguin, Landau, Verwey and Overbeek (DLVO). As an application of these findings, it will be illustrated how colloid facilitated transport can be understood on a quantitative basis within a natural soil environment.

8-15
**Influence of Alginate and Ionic Composition on the Stability of Hematite Colloids**
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Alginate is a polysaccharide ubiquitous in natural aquatic environments and engineered systems. It is very likely that alginate absorbs onto colloidal and particulate matter, influencing the fate and transport of colloids and associated pollutants in aquatic systems. An important characteristic of alginate is the formation of a cross-linked gel matrix in the presence of calcium cations. In this study, we characterize the alginate by potentiometric and complexometric titrations to determine its carboxylic acidity and availability of calcium binding sites, respectively. We then pre-adsorb synthesized hematite colloids with alginate under favorable pH conditions. The aggregation kinetics of the alginate-coated hematite colloids is determined by dynamic light scattering in the presence of monovalent (NaCl) and divalent (CaCl₂) electrolytes, and is compared with the kinetics of the bare hematite colloids. The absolute aggregation rate
constants for both the bare and coated colloids under favorable conditions at high NaCl concentrations are similar, indicating that they share similar aggregation mechanism of electrostatic destabilization. In the presence of calcium ions, the growth of the alginate-coated hematite aggregates is much faster than in sodium ions, implying that the aggregation mechanisms are different. A discussion of the mechanisms involving the role of alginate will be presented.

8-16
Effect of Monovalent and Divalent Electrolytes on the Adsorption of Polysaccharides on Solid Surfaces in Aquatic Systems
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Polysaccharides play an important role in the fouling of surfaces in natural and engineered aquatic systems due to their strong adsorptive properties. These highly charged polyelectrolytes adsorb in compact layers, rendering cleaning of the fouled devices difficult and expensive. In this study, adsorption of two model polysaccharides, polygalacturonic acid (PGA) and sodium alginate, was examined as a function of ionic strength and calcium ion concentration utilizing quartz crystal microbalance with dissipation (QCM-D). The variation of frequency, which corresponds to the adsorbed polyelectrolyte mass, was analyzed following incremental increases in the ionic strength and consecutive additions of polysaccharides. PGA had very similar adsorption patterns as alginate in absence of divalent cations. In presence of calcium, both polysaccharides demonstrated significant complexation with calcium ions, showing 20 and 10 times greater initial adsorption of PGA and alginate, respectively, than scenarios without calcium. In most cases, the increase of ionic strength above 100 mM caused a decrease in the adsorbed mass, suggesting compaction or destruction of the adsorbed polyelectrolyte layer. The observed adsorption behaviors are discussed in terms of the structure and chemical properties of the two polysaccharides.

8-17
Effect of Chemical and Hydrodynamic Parameters on Interfacial Retention of Colloids in Unsaturated Micromodel Channel
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Transport of colloids and colloid-facilitated transport of contaminants in soil and groundwater aquifers have been widely acknowledged in the literature. Mineral-grain attachment, air-water interface and contact line retention are the major mechanisms determining the extent of colloidal transport in unsaturated porous media. Although unsaturated colloidal transport has been extensively studied in past years, its complete understanding is pending. The present study investigates the parameters that affect the behavior of colloids on air-water interface and contact line. The principal elements of the employed experimental system include a glass channel micromodel and laser scanning confocal microscope, which allows the visualization of colloidal systems at the pore scale. The study includes both dynamic (flow) and static experiments. The flow experiments showed strong influence of hydrodynamic conditions both on air-water
interface and contact line retention whereas the static experiments reflected the effect of solution chemistry. Applying to natural dynamic systems, the combined effect of chemical and hydrodynamic conditions on colloidal retention in soil is expected.

8-18

Direct observation of Colloid Deposition at Grain-Grain Contacts in Porous Media Using X-ray Microtomography

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Colloid deposition at grain-grain contacts is potentially important in porous media. However, common approaches used to examine colloid deposition (e.g. column experiments) do not differentiate environments of deposition in porous media. In this work, direction observation of the environment of deposition was performed using x-ray microtomography (XMT), a technique that yields exact 3-D representation of the pore domain with a spatial resolution down to 5 micrometers. Near neutrally buoyant microspheres “visible” to x-rays were prepared. Microsphere suspensions (2.0×10^3 particle·mL^{-1}) were injected into a small column packed with glass beads (average diameter 800 μm). Following injection, XMT images were obtained and deposited microspheres were directly characterized. The extent of deposition at grain-grain contacts was examined with changes in fluid velocity and microsphere size. The maximum number of microspheres deposited at grain-grain contacts was located increasingly down-gradient of the column inlet with increasing flow velocity, indicating the reversibility of deposition at grain-grain contacts.

8-19

Secondary Minimum Sorption of Microorganisms: Unexpected Prevalence, Implications and Modeling

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When colloidal particles and collector surfaces have the same charge, deposition is termed “unfavorable” due to large electrostatic energy barriers inhibiting sorption in the primary minimum. DLVO calculations often reveal the presence of a secondary minimum (F_{2-min}) that can trap colloids, but F_{2-min} sorption is considered unlikely at low ionic strengths. However, we observed reversible F_{2-min} sorption of Cryptosporidium parvum oocysts to clean silica sand at = 0.0001 M NaCl. F_{2-min} sorption may explain (1) unexpected removal previously attributed to phenomena such as surface heterogeneities, straining, steric interactions or hydrophobic forces, and (2) unexpected release of colloids that occur in the presence of slight chemistry changes or mechanical inputs of energy. The latter may occur because the energy well at the secondary minimum can be quite shallow (e.g., = 1-2 k_BT). A new conceptual model for understanding colloid filtration in unfavorable conditions was developed by expanding on the work of Hahn and O’Melia (2004) relating the depth of the F_{2-min} and the Maxwell distribution of colloid energies to detachment probability. Rather than calculating a collision efficiency, all collisions
were assumed to result in attachment and a distribution of detachment rates was used to simulate colloid transport in porous media.

8-20

**Force Interactions Profiles between Cryptosporidium parvum Oocysts and Silica Surfaces**

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The interaction force profile between single Cryptosporidium parvum oocysts and silica particles were measured in aqueous solutions using an atomic force microscope. The oocysts were immobilized during the measurements by entrapment in a Millipore polycarbonate membrane with 3 µm pore size. Experiments were performed in both NaCl and CaCl₂ solutions at ionic strengths ranging from 1 to 100 to mM. For both electrolytes, the decay length of the repulsive force profile, obtained via the slope of a plot of the logarithm of the interaction force versus oocyst/substrate separation, was found to be essentially independent of the ionic strength and always much larger than the expected Debye length of the system. In addition, the magnitude of the force was found to be essentially the same for both electrolytes, suggesting that the long-range repulsive forces are strictly steric in nature. The only apparent difference between experiments in the two electrolytes was that strong adhesive forces were frequently observed in the calcium solutions. Comparisons of these results with recent particle deposition studies will also be made.

8-21

**Role of Surface Proteins in the Deposition Kinetics of Cryptosporidium parvum Oocysts**

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A radial stagnation point flow system was used to investigate the influence of Cryptosporidium parvum surface properties on oocyst deposition kinetics onto an ultra pure quartz surface. In order to determine the role of oocyst surface-bound proteins in adhesion, the deposition kinetics of viable oocysts were compared with the deposition kinetics of oocysts treated with either heat or formalin. Low deposition rates and corresponding attachment efficiencies were observed with viable oocysts over the entire range of solution conditions investigated, even where DLVO theory predicts the absence of an electrostatic energy barrier. An “electrosteric” repulsion between viable Cryptosporidium and the quartz substrate, attributed to the proteins on the oocyst surface, is surmised to cause this low deposition rate. Treatment of the oocysts with either heat or formalin was found to alter the structure of the surface proteins and reduce steric repulsion with the quartz substrate. Oocyst surface proteins were then removed with a digestive enzyme (Proteinase K), and their overall effect on the oocyst electrokinetic properties, and oocyst deposition rate were determined.

8-22

**Profiles of Retained Cryptosporidium Oocysts in Porous Media – Evidence for Dual Mode Deposition**
Spatial distributions of Cryptosporidium parvum oocysts in columns packed with uniform glass-bead collectors were measured over a broad range of physicochemical conditions. Comparison of oocyst retention with results obtained using polystyrene latex particles of similar size suggest that mechanisms controlling particle deposition are the same in both systems, that is, “fast” deposition in secondary energy minima and on favorably charged surface heterogeneities, and “slow” deposition over electrostatic energy barriers. A dual deposition mode model is applied which considers the combined influence of “fast” and “slow” oocyst deposition due to the concurrent existence of favorable and unfavorable colloidal interactions. Model predictions of retained oocyst profiles and suspended oocyst concentration at the column effluent are in good agreement with experimental data. Because classic colloid filtration theory does not account for the effect of dual mode deposition (i.e., simultaneous “fast” and “slow” oocyst deposition), these observations have important implications for predictions of oocyst transport in subsurface environments, where repulsive electrostatic interactions predominate.

Influence of Nutrient Condition on the Adhesion Kinetics of Burkholderia cepacia G4g and ENV435g
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The sensitivity of Burkholderia cepacia G4g and ENV435g adhesion kinetics to nutrient condition has been observed. The kinetics of cell adhesion was investigated in a radial stagnation point flow (RSPF) system under well controlled hydrodynamics and solution chemistry conditions. Comparable adhesion kinetics were observed for the mutant (ENV435g) and wild-type (G4) grown in the same medium; however, the adhesion efficiency increased with the level of nutrient presence for both cell types. To elucidate the cause of the deposition sensitivity to nutrient condition, complimentary cell characterization techniques were conducted to evaluate the viability, hydrophobicity, electrophoretic mobility, and size of cells grown in both nutrient rich Luria broth (LB) and poor basal salts media (BSM) growth media. Additionally, the charge density, as well as the polysaccharide and protein content of the extracellular polymeric substances (EPS) were evaluated under the differing nutrient presence. Nutrient condition was found to alter cell deposition due to its impact on the EPS composition and size characteristics of the cells.

Bio-Colloid Facilitated Metal Transport in Geologic Media: Observations and Surface Complexation Modeling

Bench-scale experiments demonstrated enhanced Zn(II) and Pb(II) transport in flow-through columns packed with either iron/aluminum-oxide coated sand or limestone chips when bacteria were injected with the metal, relative to experiments performed without bacteria. In a column
packed with limestone chips, the effluent concentration of zinc injected in the presence of bacteria (*Pseudomonas stutzeri*, $8.5 \times 10^7$ cells/ml) was 8-fold higher than when no bacteria were injected. The transport of zinc in a column packed with sand was enhanced 13-fold in the presence of $1.1 \times 10^8$ cells/ml. The bacteria were pre-starved and no carbon source was present, so it is assumed that the bacteria sorbed and transported the metal independently of cellular metabolism. The pH dependence of the enhanced transport was modeled using surface complexation chemistry coupled with a transport model. The surface complexation model simulates the competition for the metal between the organic functional groups on the bacterial surfaces and the inorganic functional groups on the geologic media surfaces. The specific sorption reactions used to model the metal sorption to the bacteria and the geologic media will be discussed along with the strategy used to model bacterial transport in the framework of the contaminant transport model.

8-25
**Deposition and Re-entrainment Dynamics of Microbes and Non-Biological Colloids during Non-Perturbed Transport in Porous Media in the Presence of an Energy Barrier to Deposition**
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This presentation examines the non-perturbed deposition and re-entrainment dynamics of biological and non-biological colloids in porous media in the presence of an energy barrier to deposition at the grain surface. Deposition and re-entrainment rate coefficients were determined from numerical simulation of breakthrough-elution behavior and the profiles of retained colloids. Results are presented for non-biological and biological colloids of sizes ranging from 0.25 μm to 5 μm for transport within porous media of different angularity and roughness, under a variety of ionic strength and fluid velocity conditions. In the presence of an energy barrier, deposition efficiencies decreased with increasing fluid velocity for all colloids and conditions examined. In the presence of an energy barrier, re-entrainment rate coefficients increased with increasing fluid velocity. These results demonstrate that in the presence of an energy barrier to deposition, hydrodynamic drag mitigates deposition and drives re-entrainment of both biological and non-biological colloids. The possibility of colloid association with the primary energy minimum is considered via a balance of hydrodynamic and adhesive torques. The possibility of colloid association with the secondary energy minimum is considered via reversibility of deposition; and via parallel experiments in porous media and simple shear flow systems.

8-26
**Real-time Observation of Colloid Transport in Porous Media at Mesoscales Using Epi-fluorescence Imaging**
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The lack of direct, continuous observation of the movement of colloids in porous media limits our knowledge of the processes that control colloid transport and immobilization in these media. Here we developed a non-evasive, epi-fluorescent imaging technique to quantify the distribution of fluorescent microspheres in translucent sand at mesoscales (maximum view area of 20 cm by
20 cm). Carboxylated latex microspheres were injected into a flow cell (20 cm long by 10 cm wide by 1 cm thick) packed with clean quartz sand at various flow rates and ionic strengths, and then eluted with microsphere-free solution of identical chemistry. Nonmonotonic colloid distribution profiles were observed in all transport experiments under unfavorable deposition conditions. Direct observation and comparison of the 1-D distribution profiles at different elution times (up to 6 pore volumes) clearly showed a down-gradient movement of microspheres during elution, suggesting that the nonmonotonic distribution profiles observed in this particular study was due to the detachment of retained microspheres.

8-27
**Role of Zones of Low Hydrodynamic Drag in Colloid Deposition and Re-entrainment in Porous Media**
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Existing colloid deposition models assume that attached colloids are not subject to hydrodynamic drag, whereas recent experiments demonstrate that in the presence of electrostatic repulsion hydrodynamic drag mitigates colloid deposition and drives colloid re-entrainment. The deposition and re-entrainment behaviors of three different-sized carboxylate modified polystyrene latex microspheres were systematically examined in packed porous media and impinging jet systems under various fluid velocity conditions. Deposition efficiencies were compared between the porous media and impinging jet systems to determine the influence of zones of low hydrodynamic drag on colloid deposition. At the end of the experiments, the porous media and the impinging jet experiments were eluted with pure water to deepen the barrier to detachment from primary energy minima, and to eliminate secondary energy minima. The extent of release of retained colloids upon elution with pure water indicated the significance of primary and secondary energy minima to colloid deposition. The results indicate the importance of grain surface angularity in the generation of zones of low hydrodynamic drag that enhance colloid deposition in porous media.

8-28
**Deposition and Characterization of Nanoparticulate FeS on Quartz Surfaces for Remediation of As(III) Contaminated Groundwater**
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Nanoscale synthetic FeS (mackinawite) has been found to be effective at removing As(III) from solution under anoxic conditions over a wide range in pH values. This is due both to the large surface area of nanoscale FeS and because this form of FeS provides a readily available source of sulfide for As(III) precipitation as an As-S solid. To utilize FeS for implementation as a reactive media in permeable reactive barriers (PRB), and in order to avoid potential permeability
reduction or loss of particles that may be caused by nanoparticulate FeS forms, we have been testing the feasibility of coating quartz sand particles with nanoscale FeS. Since both quartz sand and nanoscale FeS exhibit negative surface charge over nearly the entire pH range, these particles tend to repel one another and thus present a challenge for developing effective coatings. This study reports quartz surface modifications that are being used to make it more amenable for electrostatic self-assembly by nanoscale FeS. The ultimate goal of this work is to produce a highly reactive surface FeS surface coating on quartz sand while maintaining the reactive properties of nanoscale FeS for As(III) removal from groundwater in PRB applications.

8-29
Homogeneous Nucleation in the Ambient Atmosphere
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One of the important recent findings has been that homogenous nucleation in the atmosphere is a much more common event that had been previously been recognized. Initially these events were observed in remote areas such as Hyytiälä, Finland and Mace Head, Ireland. However, recently these events have been found to occur in urban areas in the presence of a preexisting aerosol. Measurements made in Atlanta, Pittsburgh, and Rochester have shown that two types of events, plume and regional. In plume events, short term bursts of nanometer-sized particles (10 to 20 nm) are observed in the late morning/early afternoon time period. In the regional events, the nucleation burst if followed by condensational growth leading to particles in the 60 to 80 nm range. The nature of the nucleation process and the potential effect of such events on the properties of the atmospheric aerosol will be discussed.

8-30
Direct Force Measurements between Carboxylate-Modified Latex Microspheres and a Glass Surface Using Atomic Force Microscopy
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Interaction and adhesion forces between 1.0-?m carboxylate-modified polystyrene latex microspheres and a glass surface were measured directly with an atomic force microscope using the colloidal probe technique. Measurements were conducted as a function of ionic strength in two different electrolytes, NaCl and MOPS (3-(N-morpholino)-propanesulfonic acid) buffer, at pH 6.8-6.9. AFM approach curves were fitted to theoretical DLVO force curves by varying the surface potential of the microspheres. The depths of the primary minima of the fitted theoretical DLVO curves were used to estimate theoretical adhesion forces, and were compared to the pull-off forces measured by AFM. Pull-off forces measured by AFM in both electrolytes were consistently a factor of 5 to 10 lower than the pull-off forces estimated from theoretical adhesion forces obtained from DLVO curves. AFM-measured pull-off forces decreased with increasing the ionic strength in both electrolytes, whereas the adhesion forces calculated from DLVO showed either no change or an increase with increasing the ionic strength. These observations indicate that the DLVO-based approach for determining adhesion force severely overestimates the actual adhesion force.
Development and Use of a Bioluminescent Biosensor for Assessing the Bioavailability of Organic Pollutants in Surfactant Micelles

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A direct measurement technique for microbial bioavailability was developed using a whole-cell bioluminescent biosensor, PpF1G4. To create PpF1G4, bioluminescent reporter genes (lux) were placed under the control of the promoter region of the solvent efflux pump genes (sep) in Pseudomonas putida F1. Biosensor PpF1G4 produces a bioluminescent response to a wide range of aromatic compounds. PpF1G4 was used to evaluate how three nonionic surfactants (Triton X-100, Brij 30 and Brij 35) influence the bioavailability of three different organic pollutants (toluene, naphthalene, and phenanthrene) present as individual compounds in solution in excess of solubility as well as the bioavailability of multiple solutes partitioned from non-aqueous phase liquid multi-component mixtures such as coal tar and creosote. The increased bioluminescent response of PpF1G4 in micellar solutions of Triton X-100 and Brij 35 indicated higher intracellular concentrations of the test compounds, toluene, naphthalene and phenanthrene, compared to control systems with no surfactants present. The above results and transmission electron microscope images of PpF1G4 in micellar surfactant solutions suggest that nonionic surfactants may enhance bioavailability and biodegradation rates by increasing the mass flux of substrates present in the micellar pseudophase to the cells through mechanisms that do not involve visible changes to membrane permeability.

(CdSe)ZnS Quantum Dots and Organophosphorus Hydrolase Bioconjugate for Paraoxon Detection

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This work was focused on detection of paraoxon using a bioconjugate of (CdSe)ZnS core-shell quantum dots (QDs) and organophosphorus hydrolase (OPH). The OPH was coupled to (CdSe)ZnS core-shell QDs through electrostatic interaction between negatively charged QDs surfaces and the positively charged protein side chain and ending groups (-NH₂). Detectable secondary structure changes were observed by Circular Dichroism (CD) spectroscopy when the OPH/QDs bioconjugate was exposed to organophosphorus compounds such as paraoxon. Photoluminescence (PL) spectroscopic study showed that the PL intensity of the OPH/QDs bioconjugate was quenched in the presence of paraoxon. The overall quenching percentage as a function of paraoxon concentration matched very well with the Michaelis-Menten equation. This result indicated that the quenching of PL intensity was caused by the conformational change in the enzyme, which is confirmed by CD measurements. The detection limit of paraoxon concentration using OPH/QDs bioconjugate was about 10⁻⁸ M. No further increase of sensitivity was achieved when the molar ratio of OPH to QDs was greater than 20 because the QDs surface
was saturated by OPH. These properties make the OPH/QDs bioconjugate a promising step towards detection of organophosphorus compounds.

8-33
Mixed-Order Modeling of Simultaneous Particle and Dissolved Substrate Removal by Aerobic Biological Film Wastewater Treatment Systems
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Several mechanistic models have been developed to describe the kinetics of dissolved substrate utilization by biological films, or biofilms. These models, however, have limited application when the primary constituent of chemical oxygen demand in domestic wastewaters is organic particles. Recent research has demonstrated that frequently a small fraction of the total chemical oxygen demand (TCOD) in raw sewage and primary effluents is dissolved. Therefore, there is a need to develop a mathematical expression capable of describing the removal of simultaneous particulate and dissolved organic matter from wastewaters. The primary objective of this research project is to study the kinetics of particulate COD (PCOD) removal from wastewaters by biological films and apply the respective kinetic expression to a model that includes phenomena such as diffusion and reaction of dissolved substrate inside the biofilm, and the simultaneous flocculation of organic particles at the external film surface. The resulting mixed-order model is validated using a laboratory scale completely mixed biofilm reactor.

8-34
High Performance Carbon Honeycomb for Air Separation
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Carbon adsorbent materials are of paramount importance in environmental technology, from gas purification and separation to gas storage or catalyst supports. These processes rely on specific pore size distributions that contribute to selective adsorption via size exclusion. Low temperature nitrogen adsorption, small angle X-ray scattering (SAXS) and frequency response (FR) measurements are reported for carbon prepared by heating wood from scotch fir (Pinus sylvestris) in an inert atmosphere to temperatures in the range 600°C ≤ T = 1000°C. The honeycomb structure, conserved from the original wood, provides easy access for gas adsorption and air separation applications. The surface area measured by gas adsorption, $S_{BET}$, and the microporosity both increase with increasing $T$, while significant mesoporosity develops at 1000°C. Although the samples are highly anisotropic at distance scales greater than 10 nm, the specific surface area $S_X$ derived from SAXS is isotropic within experimental error. FR measurements of the adsorption rate of nitrogen and oxygen reveal strong selectivity in favour of oxygen for the 700°C sample, whose characteristic slit width is approximately 0.33 nm. For $T$=1000°C, the slit width doubles and the selectivity disappears.