

STI Product for DOE award No. DE-FG02-08ER15925

The purpose of award no. DE-FG02-08ER15925 was to fund travel for students to present at the Fall 2007 American Geophysical Meeting. This was done successfully, and five students (Bin Xie, Qiaona Hu, Katie Schreiner, Daria Kibanova, and Frank-Andreas Weber) gave excellent oral and poster presentations at the meeting. The following are the conference abstracts for their presentations.

B33C-1434

Effect of Natural Organic Matter (NOM) on Properties and Mobility of Aqueous Fullerene Nanoparticles (nC60)

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C60 fullerene and its derivatives have been used in a number of consumer products and the predicted industrial- scale production of fullerene reaches tons per year. Aqueous fullerene nanoparticles (nC60) could be formed through direct contact of fullerene powder with water or through organic solvent exchange. Existing toxicity data of nC60 indicate that industrial-scale production of fullerene poses a potential threat to the environment. There is a need to evaluate the fate and transport of nC60 in the aqueous environment and its subsequent impact on the bio- and eco- systems. Our study aims to determine the effect of natural organic matter (NOM) on the nC60 entry pathway, physicochemical properties, deposition and mobility in the aqueous phase. Experimental conditions cover those typical of natural waters. Stable nC60 suspensions formed under four different conditions in the presence and absence of two major NOM components, humic acid (HA) and fulvic acid (FA), were thoroughly characterized for particle size, morphology, electrophoretic mobility, and UV absorbance. nC60 deposition experiments were carried out in parallel cross-flow chambers monitored by quartz crystal microbalance (QCM) and the nC60 mass deposition kinetics was studied in the absence and presence of NOM. Our study found that the size, structure and surface properties of readily formed nC60 changed fundamentally upon addition of NOM at environmental concentrations. For example, nC60 prepared through dissolution and removal of toluene solvent by sonication decreased in particle size, and the degree of particle size reduction was a function of solution chemistries. Bulk phase fullerene powder was directly dispersed into the aqueous phase as stable nC60 colloidal suspensions in presence of NOM at environmental concentrations in less than three days. In both cases, extremely small nC60 nanoparticles with diameter less than 10 nm were prevalently formed at specific solution conditions. The nC60 mass deposition followed zero-order kinetics onto silicon dioxide surface, at an nC60 concentration of 3 mg/L regardless of the NOM concentration (0 – 20 mg/L). The nC60 mass deposition rate decreased gradually in presence of increasing amount of NOM. For example in a solution condition of 10 mM CaCl₂, nC60 was deposited onto silicon dioxide surface at a rate of 24 nghr⁻¹ without

any NOM, yet the rate was decreased to 20 ng·hr⁻¹ in presence of 10 mg/L HA, and was further decreased to only 10 ng·hr⁻¹ in presence of 20 mg/L HA. Our study indicates that NOM significantly increases the stability and mobility of nC₆₀ nanoparticles in the aqueous environment.

B33C-1438

Surface Energetics of Calcite {10-14} Faces upon the Adsorption of succinic Acid

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Interactions of calcite with carboxylic acids occur widely and play an important role in many natural processes such as biomineralization and metal ion sequestration. The main contributor to the adsorption energy is the electrostatic interaction between the deprotonated carboxylic group of the organic acid and Ca²⁺ ions on the mineral surface. Although a number of experimental studies have identified the distribution of adsorption sites on calcite, the energetics of the surfaces of this mineral and the orientation of the organic molecules after the adsorption is still poorly understood. We have used empirical-potential methods to calculate calcite step energies for different step directions on {10-14} surfaces. In the presence of succinic acid (SUC), the less common and polar [421] and [010] directions develop and are shown to be more stable than the periodic bond chain directions. Three different adsorption cases were tested for each step: (i) one SUC molecule in the center of the step, (ii) a neutral SUC molecules chain along the step, (iii) a deprotonated SUC molecules chain along the step. These results indicate that SUC stabilizes steps in the directions parallel to [421] and [010] by lowering the step free energies. Adsorption energies of SUC were calculated along different kinds of steps with decreasing numbers of SUC molecules. The results showed a positive correlation between the number of SUC molecules and the stability of steps along [421] and [010] directions, and an insignificant dependence of step stability upon the amount of SUC molecules for cleavage directions.

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The Environmental Fate of C₆₀ Fullerenes: A Holistic Approach

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The manufacture and use of carbon-based nanoparticles, for which C60 fullerenes can be considered a proxy, has grown exponentially in the past decade, and nanotechnology is now a multi-billion dollar industry, spanning disciplines such as cosmetics, biotechnology, and agriculture. Despite this, almost nothing is known of the fate of these compounds in the environment. Based upon the strong radical scavenging properties of many of these substances there are a variety of microbial and photochemical-mediated oxidative fates that will transform the physicochemical properties and control the residence time of these compounds in nature. It is essential that these fates, as well as the fates of the products of the degradation of carbon nanoparticles, are known. For instance, conversion of C60 fullerenes to hydroxylated or carboxylated analogs will shift the manner in which they partition between soils and sediments and water as well as how they interact with cell membranes. This paper combines our findings on the microbial activity of C60 fullerenes, one of the most common types of manufactured carbon nanoparticles, along with recent literature to develop potential chemical decay trajectories in oxidative environmental settings. We show what is known about the environmental fate of this type of nanomaterial and also areas where further research is needed.

B33C-1436

Photocatalytic properties of Small Sized TiO2 Supported on Clays for the Degradation of Indoor Pollutants: Toluene and Limonene.

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Novel materials for the degradation of hydrophobic organic pollutants by photocatalytic oxidation were developed. Intercalation of TiO₂ on clays provide favorable properties to the photocatalyst due to the adsorption properties of the clay, its content of mesopores that enables pollutant trapping and its further interaction with TiO₂, leading to

mineralization. Particularly, we are interested in hydrophobic pollutants for which bare TiO₂ had been shown less effective than for polar species. Synthesis was carried out by the sol-gel method using titanium isopropoxide (Ti(OC₃H₇)₄) as precursor; the formation of anatase phase was achieved by hydrothermal treatment. Clays used were Hectorite [SHCa-1, Na_{0.4}Mg_{2.7}Li_{0.3}Si₄O₁₀(OH)₂] from San Bernardino Country, California, USA and Kaolinite [KGa-1b, Al₂Si₂O₅(OH)₄] from Washington Country, Georgia, USA. Samples characterization was conducted using XRD, SEM, XPS, ICP-OES. Our results showed a strong intercalation of TiO₂ on hectorite and a poor one on kaolinite. Nanoparticle size obtained on hectorite was of 9.6 nm compared to 17.39 nm of commercial TiO₂ (Degussa P25). Photocatalytic experiments were realized by the FTIR-ATR technique monitoring the concentration of the organic compound on the surface of the material. Results were compared with commercial TiO₂ (Degussa P25). For limonene bare TiO₂ showed better degradation rates, while for toluene, degradation rates using TiO₂ supported on clays were higher.

B32A-03

Biomineralization of Metallic Copper and Copper Sulfide Nanomaterials in a Flooded Soil: Impact on Contaminant Mobility

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Colloidal nanomaterials may enhance the mobility of strongly sorbing contaminants that are otherwise immobile in soils and sediments. We investigated the formation of biogenic nanomaterials in a contaminated wetland soil upon flooding and microbially-mediated soil reduction using microcosm experiments. Combining electron microscopy and X-ray absorption spectroscopy, we characterized the newly formed nanomaterials and evaluated their effect on the mobility of selected contaminants (Cu, Cd, Pb). In the pore water of the flooded soil, we observed the formation of <20 nm metallic Cu(0) nanocrystals associated with bacterial cells. The Cu(0) nanocrystals grew in size until the onset of microbial sulfate respiration, when Cu(0) started to transform into poorly crystalline hollow Cu sulfide structures on bacteria. Concurrently, we observed the precipitation of <40 nm Cu sulfide nanoparticles dispersed in the pore water. Both Cu sulfide hollow spheres and nanoparticles were apparently mobile and contained substantial quantities of Cd and Pb in addition to Cu, dominating their respective pore water speciation. Over extended periods of flooding, the colloids were slowly removed by deposition following apparent first-order kinetics. We have conducted additional experiments to elucidate the formation mechanism of the bacteria-associated nanomaterials observed. First evidence

suggests that the biomineralization of the Cu(0) nanocrystals occurs when Cu(I) released by bacteria, likely exported by homeostasis proteins, disproportionates on the outer cell membrane. Their transformation into hollow structures upon reaction with sulfide is interpreted to result from inward diffusion of vacancies balancing outward diffusing Cu in a Kirkendall-like process. Our results demonstrate that the formation of mobile Cu sulfide colloids enhances Cu, Cd, and Pb mobility in the flooded soil. The findings thus point to a novel pathway for the translocation of chalcogenic contaminants from wetland soils to adjacent surface and groundwater bodies.