DIVISION OF ENVIRONMENTAL CHEMISTRY

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WEDNESDAY MORNING

Emerging Environmental Technologies towards a Cleaner and Sustainable Society

V. Shah and P. Bishop, *Organizers*
V. K. Sharma, *Presiding*

8:30 — Introductory Remarks.

8:35 —70. Aging study on the structure of Fe^0-nanoparticles stabilized using inert gases: Characterization and reactivity. **Q. Wang**, H. Choi

8:55 —71. Role of ferrate(VI) technology in a cleaner and sustainable society. **V. K. Sharma**, R. Yngard, G. Anquandah, E. Casbeer, Y. Fanfan, T. Hilton, L. Chambre, A. Al-Abduly, M. Sohn, D. A. Knight

9:15 —72. Arsenic removal using titanium dioxide nanoparticles: Macroscopic and spectroscopic evaluation. **S. R. Al-Abed**, G. Jegadeesan, H. Choi, D. D. Dionysiou

9:35 —73. Effect of nanosized metal oxides on oxidation of aromatic compounds by iron oxides. **H. Zhang**, F. J. Murillo, S. Taujale, P. Bick

9:55 — Intermission.

10:05 —74. Impact of nanoscale zero-valent iron treatment on the geochemistry and microbial diversity of trichloroethylene contaminated aquifers. **T. L. Kirschling**, E. G. Minkley Jr., G. V. Lowry, R. D. Tilton

10:25 —75. Nanoparticles and nanostructures for environmental catalysis and photocatalysis. **A. Orlov**

10:45 —76. Visible light photocatalytic activity by NMP solvent treatment of polymorphic titania. **S. Kaewgun**, D. Mckinney, J. White, A. Smith, M. Tinker, J. Ziska, B. I. Lee

ABSTRACTS

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Aging study on the structure of Fe^0-nanoparticles stabilized using inert gases: Characterization and reactivity

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Inert gases, including argon, nitrogen, and carbon dioxide, were utilized to stabilize synthesized Fe^0-nanoparticles after lyophilization to prevent self-ignition. In addition, aging effect was investigated for these stabilized Fe^0-nanoparticles both in humid and dry conditions. Particles' shapes, sizes, and structures were characterized for these fresh and aged Fe^0-nanoparticles using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area and porosity analyzer, transmission electronic microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX). Even though aged Fe^0-nanoparticles were opened to the atmosphere, the Fe^0 content in these aged Fe^0-nanoparticles did not change significantly, which was proved by XRD and EDX analysis. Reactivity of fresh Fe^0-nanoparticles stabilized using inert gases for bromate reduction is more than 99.5% after 20 min, which is much higher than micro-sized ZVI. However, for the aged Fe^0-nanoparticles, the reactivity decreased as aging time increasing; additionally, the reactivity of Fe^0-nanoparticles stored in a humid condition decreased much more than that of Fe^0-nanoparticles stored in a dry condition. The observed results revealed that recovery and recrystallization happened in the aged Fe^0-nanoparticles at room temperature instead of a well-known theory that recrystallization and annealing happen at a high temperature.

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Role of ferrate(VI) technology in a cleaner and sustainable society

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Iron commonly exists in the 0, +2, and +3 oxidation states; however, in a strong oxidizing environment, higher oxidation states of iron such as +4, +5 and +6, called

ferrates can be produced. In recent years, the +6 oxidation state of iron in the form of tetraoxo-ferrate(VI) anion, ferrate(VI) ($Fe^{VI}O_4^{2-}$), has received much attention because of its possible usefulness in green organic synthesis, “super-iron” batteries, and environmentally-friendly wastewater treatment processes. Ferrate(VI) fulfills the critical need for a green chemical that can address global issues such as energy production and the availability of a safe and adequate water quality. Ferrate(VI) is highly efficient in treating a wide range of contaminants such as arsenic, endocrine disrupting chemicals (EDCs), pharmaceuticals, and emerging microorganisms without producing toxic side reactions or byproducts. The potential role of ferrates in biotechnology, nanotechnology, and innovative water treatment technology will be presented.

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Arsenic removal using titanium dioxide nanoparticles: Macroscopic and spectroscopic evaluation

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In this study, we examined the sorption of arsenite (As(III)) and arsenate (As(V)) on TiO_2 nanoparticles, produced *via* sol-gel synthesis, using a combination of macroscopic and spectroscopic investigations. Arsenic adsorption indicated that pH was not a deterrent for As(III) sorption on the amorphous TiO_2, with more than 90% removal observed for all pH. However, As(V) removal decreased significantly beyond pH 7.0. Macroscopic investigations on arsenic sorption indicated that maximum As(V) coverage on both crystalline and amorphous TiO_2 occurred in the pH range of 3.8-6.5. The effect of pH on As(III) sorption onto amorphous TiO_2 was less pronounced, in comparison to crystalline TiO_2. XAS analysis provided evidence of partial As(III) oxidation on amorphous TiO_2 and not on the crystalline TiO_2, likely due to the surface chemistry of the particles and the presence/absence of surface hydroxyl groups. Electrophoretic mobility measurements and XAS analysis indicated that As(III) and As(V) form binuclear bidentate inner-sphere complexes with amorphous. As(III) and As(V) sorption isotherms indicated that sorption capacities of the different TiO_2 polymorphs were dependent on the sorption site density, surface area (particle size) and crystalline structure. When surface coverages were normalized to specific surface areas, crystalline TiO_2 appeared to exhibit higher capacities. However, a reverse trend was observed when arsenic sorption was expressed on a per unit mass basis. The results suggested that high surface area amorphous TiO_2 particles could dramatically increase both As(III) and As(V) sorption capacities in water treatment systems.

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Effect of nanosized metal oxides on oxidation of aromatic compounds by iron oxides

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The increasing energy crisis emphasizes the need to develop clean coal technology. The utilization of coal includes long-distance transport of these materials in pipelines, which represents a complex system containing iron oxides (formed through pipeline corrosion), nano-sized metal oxides (as part of the coal minerals), and phenols and anilines (common compositions in coal). Previous studies have systematically studied the oxidation of aromatic compounds by iron and manganese oxides. Our results showed that, in a system containing both iron oxides and nano-sized metal oxides such as Al, Si or Ti oxides, phenols and anilines underwent both oxidation (by iron oxides) and adsorption (towards the metal oxides). The adsorption by the second metal oxide affected the oxidation kinetics of the target compounds by iron oxides to different extents. The results obtained in this research will greatly enhance the depth of understanding of the transformation of aromatic compounds at mixed oxide-water interfaces.

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Impact of nanoscale zero-valent iron treatment on the geochemistry and microbial diversity of trichloroethylene contaminated aquifers

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Nanoscale zero valent iron (NZVI) is a new and promising technology for the *in situ* treatment of trichloroethylene (TCE) contamination. These nano-sized particles rapidly reduce TCE to nontoxic products. Before NZVI treatments are implemented on a large scale, the impact on the environment must be considered. Of particular concern is the bactericidal effect that NZVI exhibits in planktonic cultures. This project seeks to determine if the addition of NZVI will decrease the soil microbial diversity, as well as to describe how NZVI alters the site geochemistry. Changes in microbial diversity and geochemistry were monitored in soil microcosms from three different TCE contaminated

sites over a period of eight months. Over this time period, no toxic effect on the overall bacterial population was observed. The reducing conditions and hydrogen production created by NZVI corrosion make it an attractive treatment to combine with bioaugmentation for enhanced TCE degradation.

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Nanoparticles and nanostructures for environmental catalysis and photocatalysis

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This project developed several promising materials for gas-phase decomposition of volatile organic compounds (VOCs) and liquid-phase decomposition of chlorinated organics. We utilized high surface area materials, such SBA-15 mesoporous molecular sieves, to support transition metal catalysts. More specifically, we studied manganese modified SBA-15 in decomposition of propene and titanium modified SBA-15 for photocatalytic degradation of 4-chlorophenol. We characterized these nanostructured materials by solid state NMR, XRD, BET surface area, FTIR and electron microscopy. Both catalysts showed a significant activity for environmental degradation of the pollutants. Additionally, we produced metal nanoparticles modified and heteroatoms doped photocatalysts for UV and visible light decomposition of organics. The catalysts showed a significant improvement of activity as compared to unmodified materials. We also characterized the interactions of pollutants, such as 4-chlorophenol, with the catalyst surfaces by using various environmental molecular science techniques, such as NEXAFS, XPS and UPS.

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Visible light photocatalytic activity by NMP solvent treatment of polymorphic titania

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Visible light active polymorphic titania nanoparticles were prepared by post-treatment of a water-based ambient condition sol (WACS) using a solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent. SACS samples were calcined in either air or nitrogen atmosphere under various conditions. Nitrogen

incorporation of SACS titania was investigated by CHN analysis and X-ray photoelectron spectroscopy (XPS). All samples were also characterized by X-ray diffraction, N_2 physisorption, UV-Vis absorption spectroscopy, and TEM and compared to a commercial titania powder, Degussa P25. The calcination conditions, especially the temperature and calcination atmosphere, have an influence on the BET surface area, crystallite size, titania phase content, and photocatalytic activity, evaluated by the degradation of methyl orange dye under visible light irradiation. SACS calcined in air at 200^{o}C for 2 hours showed the best visible light activated photocatalytic performance in this study. The enhanced visible light photocatalytic activity is explained based on the crystallography and surface morphology.