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New Applications of Solid Phase Adsorbents

E. Rosenberg, *Organizer*

ABSTRACTS

IEC 1

Variables in the design of ion-complexing polymer-supported reagents: Hydrogen bonding as a switching mechanism in the binding of lanthanide ions from highly acidic solutions

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Hydrogen bonding can attenuate the ion-complexing properties of immobilized ligands. Earlier research has established this with a series of phosphate-modified polyols, including pentaerythritol and glycerol. Current research has extended this to a series of amide-based ligands. The example of immobilized tetramethylmalonamide (TMMA) will be detailed. The substrates are lanthanide ions in 0.001 M - 8 M HCl and HNO₃ solutions. In HCl, distribution coefficients are low from 0.001 to 2 M, increase in 4 M and 6 M HCl, then decrease in 8 M HCl. The affinity sequence in 6 M HCl is Tb > Dy > Eu > Gd > Ho > Sm > Er > Tm > Yb > Lu > Nd > Ce > La. The complexation mechanism is ion-pairing: at acid concentrations exceeding 2 M, protonation of the amide occurs at the carbonyl oxygen which is stabilized by the adjacent carbonyl; this then switches on an iminium moiety that becomes the site of electrostatic attraction to the anionic lanthanide chlorocomplex and releases waters of hydration.

IEC 2

Diamond-based materials for liquid chromatography

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Diamond is a material that may become important in chromatography because of its remarkable physical and chemical properties. Recently, we have described the amine functionalization of diamond with poly(allylamine), and the alkylation of diamond with di-tert-amylperoxide. However, one significant limitation to diamond's use in chromatography is its lack of porosity. In this contribution we describe a layer-by-layer approach to creating core-shell diamond particles. This process begins with the adsorption of an amine-containing polymer to the diamond surface, followed by the adsorption of nanodiamond particles. This process is continued in an alternating fashion to build up multiple polymer-nanodiamond layers onto the surfaces of core diamond particles, which results in materials that have high surface areas. These enhancements in physical properties are confirmed by BET isotherm measurements, FTIR, and capacity measurements from solid phase extraction. We demonstrate formation of these particles on two size scales using i) ca. 50 micrometer diamond core particles with ca. 250 nm shell diamond particles for solid phase extraction, and ii) ca. 5 micrometer diamond core particles with ca. 10 nm shell particles for high performance liquid chromatography.

IEC 3

Efficient and selective removal of metal contaminants from water using functionalized crosslinked chitosan-based adsorbants

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CCT is focused on metal removal from drinking water as well as metal recovery from industrial water discharge. Our current efforts are focused on chitosan, a well

researched material that has yet to be commercialized as an adsorbent for water purification. CCT is developing a chitosan material with sufficient physical strength and metal removal capacity to be of commercial interest. New high capacity metal removal adsorbents employing functionalized and cross-linked chitosan are discussed. In one example water from the Berkeley Pit, MT is treated with a new dehydrated CCT chitosan. The results show nearly quantitative removal of copper (initially 128 ppm) with high selectivity over iron (only ca. 2% removal from 635ppm) and in the presence of high concentration (22,200 ppm) of sulfate. Use of a similar CCT chitosan on industrial discharge from Beal Mtn, MT shows 73% removal of cobalt and only 1% of iron in 1,440 ppm sulfate. In-house testing shows that the new materials also exhibit high affinity for lead and selenium. Work continues on evaluating CCT chitosan adsorption performance at ppb levels of heavy metals such as mercury and arsenic as are commonly found in the natural environments of various regions.

IEC 4

Supramolecular approach to ligand and functional material design for toxic metal ion sorption: A route to regenerable materials?

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Many of the “main-group” elements – including arsenic, tin and lead – are legendary for their toxicity. Our lab has been developing a supramolecular approach to design specific chelators for the main group ions. The design strategy targets the unusual coordination geometry of these toxic ions using dithiol-based ligands, which provides for specificity in metal ion binding. The strategy also relies on high-yielding self-assembly reactions to form very stable complexes. Solution studies reveal these organic ligands are selective for arsenic and other Group 15 elements. This paper will highlight results from these basic science pursuits, providing an introduction to how these studies led into the development of functional nanomaterials for water purification. This new class of sorbent material, which exhibits exceptional metal capture from contaminated natural water, features similar aromatic thiol ligands reversibly bound to functionalized mesoporous silica through noncovalent interactions. The reversible nature of the ligand loading provides the potential for recharging of the spent material.