

Project Title: Rational Synthesis of Imprinted Organofunctional Sol-gel Materials for Toxic Metal Separation (60096)

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Progress report:

RESEARCH OBJECTIVE

The objective of this program is to rationally design and synthesize imprinted sol-gel SiO₂ and SiO₂-MO₂ (M = Ti, Zr) materials containing Si-X-L binding groups through template approaches and develop a scientific basis for metal ion binding and recognition by such tailored hybrid inorganic-organic materials. These hydrophilic oxide-based materials are expected to remove metal ions from aqueous solutions intrinsically fast (in comparison to hydrophobic organic polymers), and the imprinted binding sites are expected to exhibit enhanced recognition and binding of target RCRA metal ions.

RESEARCH PROGRESS AND IMPLICATIONS

As of February 2000, the research progress in five months (9/15/99 - 2/15/00) of this three-year project is summarized here. We have successfully prepared sol-gels grafted or doped with organic ligands specific for binding targeted RCRA metal ions Cu²⁺, Hg²⁺, UO₂²⁺, Sr²⁺, and Cs⁺. When these organofunctional sol-gels are exposed to solutions containing the targets, they quickly remove them from aqueous solutions. In many such sol-gels, the metal ions absorbed in the sol-gels can be easily removed to regenerate the organofunctional sol-gels for subsequent cycles of metal ion removal. Work during this period has focused on the following areas: (1) Study of the critical factors necessary for the efficient preparation of highly selective imprint mesoporous sol-gels; (2) Developing new ligand as well as grafting and doping procedures for producing mesoporous hybrid sol-gel materials with anchored ligands; and (3) Investigations of bimetallic (Ti/Si) oxide systems for the removal of Cs⁺ and UO₂²⁺ ions from aqueous solution.

(1) Imprinting Design and Methodology for Sol-Gels. We have conducted an extensive series of investigations to elucidate the critical factors involved in the efficient preparation of imprinted, hybrid sol-gel based sorbents designed to selectively remove target RCRA metal ions. Three different procedures are currently under investigation which can be considered first, second and third generation imprinting procedures. First generation imprinting involves anchoring a templated collection of ligands around a target [Cu²⁺, Hg²⁺, Cs⁺, UO₂²⁺ (depleted)] on a preformed silica surface. Preliminary studies using diamine reagents for the selective binding of Cu²⁺ ions gave rise to relative selective coefficients $k = [k = k_{\text{imprint-coated}} / k_{\text{control}}; k = K_{\text{d (target)}} / K_{\text{d (Zn competitor)}}]$ as large as 40 which, to our knowledge, are the largest values currently reported for imprinted metal ion sorbents. Second generation imprinting studies involve anchoring the ligand-target template onto the pore surfaces of mesoporous sol-gels via ion exchange equilibria between the charged template aggregate and surfactant molecules used to develop mesoporosity. This procedure bypasses the need to remove the surfactant in a separate step and preconditioning of the support surface for grafting ligand-target templates. Preliminary studies with amine-copper templates have led to high surface area sorbents effectively functionalized with higher ligand loadings than attainable by conventional coating procedures. Third generation imprinting (as known as hierarchical double-imprinting) involves combining

and controlling the adsorption process (imprint formation) and pore structure forming reactions simultaneously. Thus, while surfactant based micelles enforce mesoporosity (>20 D diameters) on the forming gel, target ion-template complexes graft into these surfaces to produce, once the metal is removed, templated cavities which are ordered on the molecular level (1-3 D). Preliminary studies with copper-amine templates have produced very selective sorbents with relative selectivity coefficients $k = (> 200)$.

(2) Direct Sol-Gel Approaches to Anchored and Doped Ligands for the Removal of Sr^{2+} , Cu^{2+} and Hg^{2+} . A substituted diaza-18-crown-6 with high affinity for Sr^{2+} has been encapsulated in sol-gels by a simple, one-step approach. The Sr^{2+} uptake studies determined the doped gels absorbed Sr^{2+} quickly with both high capacity and selectivity in the presence of excess Ca^{2+} . The loaded gels could be efficiently stripped of Sr^{2+} with a single acid wash and, after neutralization, cycled for repeated Sr^{2+} binding without loss of performance.

Commercially available ethylenediamine ligands linked to $-\text{Si}(\text{OR})_3$ groups have been used to adsorb both Cu^{2+} and Hg^{2+} ions from aqueous solution. The gels are prepared by mixing the anchored diamine ligands with $\text{Si}(\text{OMe})_4$ in water. Cu^{2+} uptake and release (under acidic conditions) were studied through several cycles. No loss of binding affinity was observed. Selectivity studies between Cu^{2+} , Zn^{2+} and Cd^{2+} showed that the grafted amine ligands bound Cu^{2+} ions in preference to either competitor.

(3) Bimetallic (Ti/Si) Oxide Systems for the Removal of Cs^+ and UO_2^{2+} . Microporous metal oxides readily adsorb uranyl ions via ion exchange reactions with surface silanols. Little is known about the adsorption properties of mesoporous analogues of these oxides. We have prepared a series of mesoporous mixed SiO_2 - TiO_2 (100/60% Si vs. Ti) and studied the binding affinity exhibited toward uranyl ion. Kinetic studies conclusively showed that uranyl uptake by mesoporous sorbents is much faster than with comparable microporous materials while total surface decreased with increasing titanium content. This result is consistent with uranyl binding primarily to TiO_2 sites on the surface.

Both coated and homogeneous mixed mesoporous SiO_2 - TiO_2 have been prepared and their affinity for Cs^+ studied. Coated materials were prepared by exposing precalcined mesoporous silica to titanium isopropoxide $\text{Ti}(\text{OPr}^i)_4$ and water while homogeneous mesoporous ($d_{\text{ave}} = 44$ D) SiO_2 - TiO_2 were prepared by mixing $\text{Si}(\text{OMe})_4$, $\text{Ti}(\text{OPr}^i)_4$, water and the neutral block copolymer Tergitol 15-s-15 surfactant together. At $\text{pH} > 10$ both coated and homogeneous Si-Ti sorbents removed >90% of the Cs^+ from solution within 1 hr (Cs^+ capacity: 0.5 mmol/g). Competition studies with both K^+ and Na^+ indicated that these sorbents removed Cs^+ selectively from solutions containing excess K^+ and Na^+ .

PLANNED ACTIVITIES

In the next 6 months we will further develop the imprint-coating techniques for both Cu^{2+} and UO_2^{2+} . Covalently grafting the functional ligands will also be assessed to link these ligands with the $-\text{Si}(\text{OR})_3$ group. Binding studies of these new ligands on sol-gels as well as imprint-coated mesoporous materials, will be performed for Hg^{2+} , Cd^{2+} , UO_2^{2+} , Cs^+ , and Sr^{2+} .

INFORMATION ACCESS

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