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Rational Synthesis of Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation

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Research Objective

The objective of this program is to rationally design and synthesize imprinted sol-gel SiO_2 and SiO_2/ $M'O_2$ (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 imprinted organofunctional materials. These hydrophilic metal 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 selectivity and affinity of target metal ions.

Research Progress and Implications

This report summarizes research after the first eight months of a three-year project. We have successfully prepared sol-gel materials grafted with organic ligands specific for binding target RCRA metal ions. When these organofunctional sol-gel materials are exposed to solutions containing target metal ions, they quickly remove the metal ions from aqueous solutions. In many such sol-gel materials, the metal ions absorbed in the sol-gel materials can be easily removed to regenerate the organofunctional sol-gel materials for subsequent cycles of metal ion removal.

Work has commenced in two main areas: (1) preliminary evaluation of target ion binding and imprinting effects, (2) studies of mesoporous materials for the separation of large metal ions such as UO_2^{2+} and TcO_4 .

Preliminary Evaluation of Target Ion Binding and Imprinting Effects

We have conducted studies to evaluate (a) the removal of target metal ions from aqueous solutions by organofunctional sol-gel materials containing grafted ligands; (b) the recovery of the metal and regeneration of the organofunctional sol-gels. The target metal ions in the preliminary evaluation are Cu^{2+}, Hg^{2+}, Sr^{2+} and UO_2^{2+}.

Cu^{2+}, Hg^{2+} and Sr^{2+} Binding Studies. These three ions are among the regulated RCRA metal ions. Ethylene diamine linked to -$Si(OMe)_3$ (N-N) was the principal reagent used in these studies. The sol-gels were prepared by first reacting the N-N ligand with M^{2+} to form a complex $M(N\text{-}N)_n^{2+}$. The complex is then mixed with a cross-linking reagent $Si(OMe)_4$ and water to give the imprinted sol-gels. Another approach is to directly mix the N-N ligand with $Si(OMe)_4$ and water without a metal template to prepare the non-imprinted sol-gels. We have improved the sol-gel formation process to give more robust materials.

Preliminary data show that metal uptake capacities of these N-N grafted sol-gels are 0.15-0.35 mmol/g for Cu^{2+}, 1.0 mmol/g for Hg^{2+} and 0.3-0.4 mmol/g for Sr^{2+}. Adding acid (HCl) readily protonates the N–N ligands and strips M^{2+} from the sol-gels. After neutralizing, the gel is again capable of removing M^{2+} from aqueous solutions. This cycle can be repeated many times. Preliminary data demonstrated that imprinted sol-gels had a higher capacity for binding Sr^{2+}.

UO_2^{2+} Binding Studies. Organofunctional silica sol-gels (imprinted and non-imprinted with UO_2^{2+}) have been prepared and their uptake of uranyl measured. Imprinting is shown to enhance the UO_2^{2+} uptake in diethylmalonate grafted sol-gels. The non-imprinted sol-gels have an affinity for uranyl

(0.03 mmol/g) similar to that of SiO_2. The imprinted samples exhibited a significantly higher affinity (0.12 mmol/g). Several silicate sol-gels grafted with other ligands (phosphonate esters, propyl amine, ethylene diamine, cyanopropyl and mercaptopropyl) have also been tested for uranyl uptake. In addition, TiO_2 and mixed SiO_2/TiO_2 sol-gels were studied. The uranyl affinity for a series of mixed SiO_2/TiO_2 sol-gels with varying Si : Ti ratios was found to increase with the amount of titanium in the sample.

Synthesis of Mesoporous Materials

Mesoporosity is critical to the performance of a sol-gel sorbent in removing metal ions such as UO_2^{2+} and TcO_4 from solution. Our research showed that the kinetics of uranyl binding by sol-gels was strongly linked to the mesoporosity of the materials. Although frequently exhibiting high total surface areas, samples that are predominately microporous bind uranyl significantly more slowly than samples that are predominantly mesoporous. Two approaches for preparing mesoporous sol-gels have been successfully developed.

Surfactant Templated Mesoporous Organofunctionalized Sol-Gels. The use of surfactants in sol-gel synthesis is known to produce mesoporous materials. The effect of surfactant templates such as cetyltrimethylammonium bromide and dodecylamine on the pore structure of organofunctional as well as SiO_2/TiO_2 mixed sol-gels has been studied. In the sol-gels grafted with phosphonate, amine or ethylenediamine, predominantly mesoporous materials were prepared (d = 20 - 25 ; surface area = 700 - 1000 m^2/g) which rapidly bound UO_2^{2+} from aqueous solution. Mesoporous mixed SiO_2/TiO_2 sol-gels which are stable to alkaline conditions were also prepared using dodecylamine as the template (d = 31 ; surface area = 760 m^2/g).

Prehydrolysis. Prehydrolysis of sol-gel precursors was investigated to inhibit the formation of microporous organofunctional sol-gels without the use of surfactants. Prehydrolysis of mixtures of $(EtO)_4Si$ and $(EtO)_3Si(vinyl)$ under acidic conditions followed by neutralization was found to give mesoporous materials (d = 36 ; surface area = 700 m^2/g). Mesoporous (d = 40 - 200) materials with surface areas between 100-300 m^2/g were also obtained by prehydrolyzing $(EtO)_4Si$ and the alkylammonium salt $(MeO)_3Si(CH_2)_3NMe_3Cl$ before gellation at neutral pH.

Our research and the preliminary results in the past eight months demonstrate that the sol-gels grafted with metal-specific ligands are potentially good sorbents for metal separation. These results have laid a solid foundation for the research in the remaining period of this project.

Planned Activities

In the next 12 months, in addition to confirming the earlier preliminary results, we will focus our attention on the capacity and selectivity of the imprinted ligand-grafted sol-gels. We will also explore grafting to sol-gels new ligands with known high affinity for target metals, and study the separation of other RCRA metals by our novel imprinted organofunctional sol-gel materials. In the final year of this project, we plan to conduct simulated waste tests involving these sol-gel materials, and optimize the overall process.