

Project ID: **60096**

Project Title: **Rational Synthesis of Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation**

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Publication Date June 15, 1999

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Progress Report

RESEARCH OBJECTIVE

The objective of this program is to rationally design and synthesize imprinted sol-gel SiO_2 and $\text{SiO}_2/\text{M}'\text{O}_2$ ($\text{M}' = \text{Ti}, \text{Zr}$) 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. Removal of metal ions from aqueous solutions by hydrophilic metal oxide-based materials is expected to be 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 in the second year of a three-year project. We have successfully prepared a variety of sol-gel materials containing grafted or entrapped ligands specific for binding target RCRA metal ions with the following current focus areas: 1) Cu^{2+} and uranyl (UO_2^{2+}) binding studies with imprinted and non-imprinted sorbents using grafted polyamine ligands; 2) Synthesis of mesoporous titanosilicate sorbents and uranyl binding studies; 3) Binding and removal of Sr^{2+} and Cs^+ ions with crown ether and calixarene-crown ether doped sol-gels; and 4) Grafted mono and polyphosphonate ligands for the binding of UO_2^{2+} and ReO_4^- (surrogate for TcO_4^-).

(1) Cu^{2+} and Uranyl (UO_2^{2+}) Binding Studies with Imprinted Sorbents. Monoamine [$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}/$; APTS] and diamine [$\text{H}_2\text{NCH}_2\text{CH}_2\text{HN}(\text{CH}_2)_3\text{Si}/$; AAPTSS] ligands have been grafted onto the surface of calcined mesoporous sol-gels in the presence of Cu^{2+} or UO_2^{2+} templating ions. Templating cations were removed, and Cu^{2+} binding experiments were conducted both alone and in the presence of competitor Zn^{2+} ions. Cu^{2+} K_d values for the imprinted samples increased by 5-6 times over the nonimprinted samples. In the presence of Zn^{2+} , $\text{Cu}(\text{AAPTSS})_2^{2+}$ -grafted sorbents showed a higher selectivity for Cu^{2+} compared to non-imprinted sorbents (Table 1). To simplify the preparation of functionalized mesoporous sorbents, we have studied the ionic exchange of a surfactant that is used in the preparation with a template complex [$\text{Cu}(\text{AAPTSS})_2^{2+}$ or $\text{UO}_2(\text{AAPTSS})_2^{2+}$] without calcining. Such sorbents have been prepared and are being evaluated.

(2) Functionalized Sol-Gels for the Separation of Copper(II) Ions. We have nearly completed our studies of sol-gel approaches to non-imprinted ligand (e.g., AATPS)-grafted sorbents for Cu^{2+} separation. These hydrophilic materials, which were easily prepared from off-the-shelf chemicals in ca. 1 h, were chosen for potentially fast kinetic processes in metal ion separation from aqueous solutions. We found, e.g., that 25 mg of AATPS-grafted gels removed Cu^{2+} (8.644 ppm) from 2.5 mL of a solution to below the detection limit of the atomic absorption spectrometer. The sol-gels loaded with Cu^{2+} ions were regenerated with an acid, and the gels could then be used in subsequent metal removal cycles. The surface areas and porosities of these sol-gels were studied, and the sol-gels were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and IR. The gel preparation processes and the time dependence of the Cu^{2+}

uptake were systematically investigated. These studies show that hydrophilic ligand-grafted sol-gels are good alternatives (to ligand-grafted organic polymers) for toxic metal separation.

(3) Synthesis of Mesoporous Titanosilicate Sorbents and Uranyl Binding Studies. Mesoporous titanosilicate sorbents were prepared by the S^{00} assembly method using dodecylamine, $\text{Si}(\text{OMe})_4$, and $\text{Ti}(\text{O}-n\text{-Bu})_4$. The kinetics of uranyl binding were significantly enhanced in mesoporous materials relative to microporous samples. Mesoporous titania exhibited the highest uranyl binding capacity.

(4) Binding of Sr^{2+} and Cs^+ with Crown Ether and Calixarene-Crown Ether Doped Sol-Gels. Disulfonated-dibenzo-18-crown-6 (DSDB18C6) has been successfully entrapped within sol-gels for Sr^{2+} removal. Sorbents doped with the ligand exhibit more Sr^{2+} uptake than non-ligand containing SiO_2 . Ligand-doped gels lowered the Sr^{2+} concentration of an 11 ppm solution to 5.8 ppm; non-ligand containing SiO_2 lowered the concentration to 8.75 ppm. The small difference in concentration change between these two sorbents could perhaps be due to the small binding affinity of the crown ligand for Sr^{2+} ; its parent compound dibenzo-18-crown-6 has $\log K \sim 1$ for Sr^{2+} . A much larger difference in the concentration change is expected for ligands with larger binding affinities. These results indicate that ligands can be easily physically encapsulated, rather than covalently bonded, within sol-gels and function to remove target metals. Calix[4]arene-18-crown-6 and calix[4]arene-(2,3-naphtho-crown-6) ether with high selectivities for Cs^+ have been synthesized and doped in sol-gels. However, leaching of the ligands from the sol-gels was observed. We are currently functionalizing these ligands and covalently binding them to sol-gel surface.

Table 1. Competitive loading of Cu^{2+} and Zn^{2+} by Cu^{2+} -imprinted sorbents buffered at pH 5.0

Type	$[\text{Cu}^{2+}]^*$	$[\text{Zn}^{2+}]^*$	% Cu^{2+} Abs	% Zn^{2+} Abs	$\text{Cu}^{2+} K_d$	$\text{Zn}^{2+} K_d$	k	k^{-1}
nonimp-APTS	0.001	0.01	35.4	63.3	55	170	0.3	-
imp-APTS	0.001	0.01	53.2	68	110	210	0.51	1.7
nonimp-AAPTS	0.001	0.001	98.5	96.6	6500	2900	2.3	-
imp-AAPTS	0.001	0.001	99.8	82.9	44000	480	91	40
nonimp-AAPTS	0.001	0.005	98.5	70	6500	230	28	-
imp-AAPTS	0.001	0.005	99.6	52.6	24000	110	220	7.7

*Initial solutions, mol/L $k' = k_{\text{imprint}} / k_{\text{nonimprint}}$

PLANNED ACTIVITIES

In the next 12 months we will further refine the imprint-coating techniques for both Cu^{2+} and uranyl. The second generation of bifunctional ligands for imprint-coating will be prepared and investigated. Ligands with higher binding affinities will be either covalently bonded or physically doped in sol-gels. Covalently grafting the calixarene-crown ethers will also be assessed. Synthetic procedures have been developed to prepare bifunctional reagents linking a $(\text{RO})_3\text{Si}$ - group to either bis-phosphonate ester groups, $-\text{CH}[\text{P}(\text{O})(\text{OR})_2]_2$, or linked phosphonate ester groups $-\text{P}(\text{O})(\text{OR})(\text{XCH}_2\text{CH}_2\text{X})\text{P}(\text{O})(\text{OR})-$. Binding studies of mono, bis and linked phosphonate ligands, as nonimprinted and imprint coatings onto mesoporous sol-gels, will be performed for UO_2^{2+} , Sr^{2+} and ReO_4^- .

INFORMATION ACCESS

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