Enhancement of Uranyl Adsorption Capacity and Selectivity on Silica Sol−Gel Glasses via Molecular Imprinting

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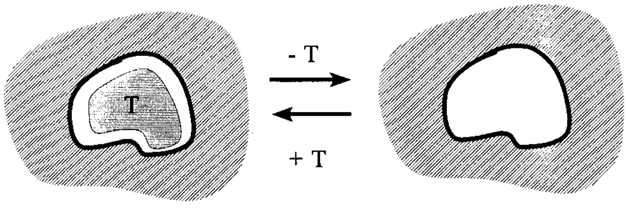
The properties of sol−gel glasses templated with uranyl ions have been investigated. Techniques have been developed to remove the template uranyl ions from silica matrixes to create uranyl-imprinted sol−gel silica glasses. A significant increase in affinity *and* selectivity of the imprinted sol−gel sorbents over control blanks has been observed while the surface areas of both remain equal. The enhanced capacity and selectivity are tentatively attributed to the change of the binding constant and the modification of the microporous structure of the sol−gel glasses induced by the imprinting technique.

Introduction

Imprinting methods (Scheme 1), based on the template approach,[1] have been used in the preparation of cross-linked polymers[1−3] as well as in silica gels[4] which possess organized surface microstructures within these solid materials. Imprinted materials combine the binding ability of specifically chosen functional groups or ligands for target substrates, with shape- and size-selective cavities imprinted into the surface of a rigid polymeric matrix by a template. Frequently, the target substrate is itself used as the template. The surface imprint is produced by the template which is present during the formation of the solid matrix. After the templating species is removed from the polymer, a predetermined arrangement of ligands and a tailored binding pocket is left. Imprinted polymers have been prepared which exhibit high selectivities and affinities for substrate binding and have been used to resolve racemates[2] and separate mixtures of metal cations.[3]

Normally, imprinting processes involve three steps: (a) selection of target molecules as templates; (b) incorporation of the templates into rigid solid networks; (c) removal of the templates leaving stable, rigid cavities that recognize the template (target) molecules. In this paper, we describe the application of imprinting techniques to the synthesis of inorganic silica sorbents which exhibit high affinity and selectivity for the binding of uranyl (UO_2^{2+}) ions.

Scheme 1. Imprinting Process via a Template (T)



Our template approach to novel inorganic imprinted sorbents is based on 3-dimensional cross-linked polymeric silica structures. The template employed in our imprinting processes is the uranyl ion (UO_2^{2+}), which is the target ion that our silica networks are designed to adsorb or bind. The solid-state silica network was prepared by the sol−gel process.[5] The sol−gel process is a technique that can be used to prepare porous, transparent oxide glasses by hydrolysis and condensation of tetraalkyl orthosilicates. Little or no heating is required, and consequently the gel can be doped or templated with molecules whose poor thermal stabilities preclude their incorporation in traditional high-temperature silica glasses.[6] Such molecules become entrapped in the growing covalent silica network rather than being chemically bound to the inorganic matrix.

The uranyl cation is a hard Lewis acid.[7] Hence, its complexation with hard bases such as oxygen-containing

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ligands is expected to be strong. In fact, the strong adsorption capacity of silica-based oxides toward uranyl ion has long been recognized.[8] These sorbents are extensively used for the sorption of uranyl ion from aqueous solutions[8] and have been proposed as potential inorganic resins to recover uranyl ion from seawater.[9] Silica-based materials are also extremely rigid due to the high degree of cross-linking found in the $(SiO_2)_n$ network.[5a] This property is very important in the design and synthesis of imprinted materials since both the size and shape of the cavities created by the template must be retained after the removal of the template. Finally, sol−gel glasses are structurally porous and can be engineered to have extremely high surface areas (200−2000 m^2/g).[5a] High accessible surface area is one factor that is related to the ion binding capacity of these materials. These considerations are the rationales that guide us in the use of the inorganic silica sol−gel matrix as an imprinting host.

Experimental Section

Literature procedures[10] were used to prepare uranyl-doped sol−gel glasses. In a typical run, 1 mL of an aqueous $UO_2(NO_3)_2 \cdot 6H_2O$ (0.1−0.05 M) solution was mixed with 1 mL of tetramethyl orthosilicate (Aldrich Chemical Co., 99%), and 1 mL of methanol (Baker Chemical Co., HPLC grade). The uranyl solution was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ into 2 N HNO_3 solution. The final mixture was cured at the ambient temperature over a period of 4 weeks. The blank control sample was prepared similarly except that no uranyl was dissolved in the nitric acid solution. Both UV−vis and fluorescence spectra of the uranyl-doped glass were very close to those of uranyl monomer that we measured before in similar sol−gel matrixes.[10a,b] Thus, we can conclude that the monomeric uranyl species is dominant in our uranyl sol−gel glasses. The uranyl distribution is quite uniform in the sol−gel glass. This conclusion is consistent with the pH (≈1) of the precursor solution used to prepare sol−gel glasses.

UV−visible spectra of the sol−gel glasses were measured by a Cary 14 scanning spectrophotometer equipped with an On-Line Instrument Systems (OLIS) data acquisition interface. Surface areas and pore volumes were measured on a Micromeritics Gas sorption system (Micromeritics Corp.). Using nitrogen as the adsorbent, 30-point adsorption isotherms were measured at 77 K after degassing the glasses at 150 °C temperature for 2 days.

Results and Discussions

Removal of Uranyl Template to Create Imprints. The adsorption of uranyl ion by silica gel sorbents can be formulated in terms of the following cation-exchange equilibrium:[8b−d]

$$\underset{[\mathrm{SiOH}]}{\equiv\mathrm{SiOH}} + \mathrm{UO_2}^{2+} \rightleftharpoons \underset{[\mathrm{UO_2}^{2+}]_s}{[\equiv\mathrm{SiO(UO_2)}]^+} + \mathrm{H}^+ \qquad (1)$$

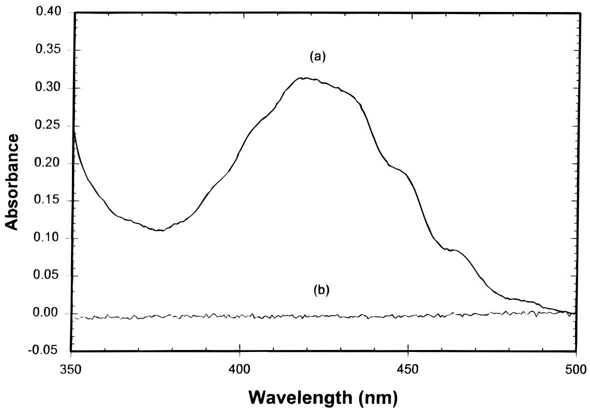

Figure 1. UV−vis spectra of uranyl-doped glass (a) before and (b) after uranyl removal.

The equilibrium constant can be expressed as

$$\frac{[\mathrm{UO_2}^{2+}]_s[\mathrm{H}^+]}{[\mathrm{UO_2}^{2+}][\mathrm{SiOH}]}F = K \qquad (2)$$

where F is the product of the activity coefficients and K the equilibrium constant. Rearranging eq 2 gives rise to

$$R_s = \frac{[\mathrm{UO_2}^{2+}]_s}{[\mathrm{UO_2}^{2+}]} = \frac{K[\mathrm{SiOH}]}{F[\mathrm{H}^+]} \approx \frac{K'}{[\mathrm{H}^+]} \qquad (3)$$

where R_s is the sorption ratio of the adsorbed uranyl ion to that in the solution. Taking logarithm of both side of eq 3 gives

$$\log R_s \approx \log K' + \mathrm{pH} \qquad (4)$$

The above equation indicates that the uptake of uranyl ion by silica sorbent materials is pH-dependent. The lower the pH of the solution, the lower the adsorption capacity of the sorbent. In fact, it is well-known that the adsorption capability of silica-based sorbents toward UO_2^{2+} is negligible below a pH of 2.[8,11] This characteristic in the uranyl binding to silicates prompted us to adopt acid washing as a method to efficiently remove the uranyl template ions from our glasses. Uranyl-free imprinted glasses were obtained by soaking the UO_2^{2+}-doped glasses with nitric acid overnight. Control blank glasses were also washed with the identical nitric acid over the same period of time to ensure that both types of glasses had identical treatments of their surfaces.

Figure 1a shows the visible region of the UV−vis spectrum of the sol−gel sample doped with uranyl template. The bands around 420 nm are attributable to the electronic charge-transfer transition of the uranyl ion.[12] The control blank sample shows no absorbance at this wavelength. Acid washing of the imprinted glass causes the 420 nm absorption bands to disappear (Figure 1b) consistent with removal of virtually all uranyl ions from the solid. The uranyl solution generated in the washing process can be reused to prepare

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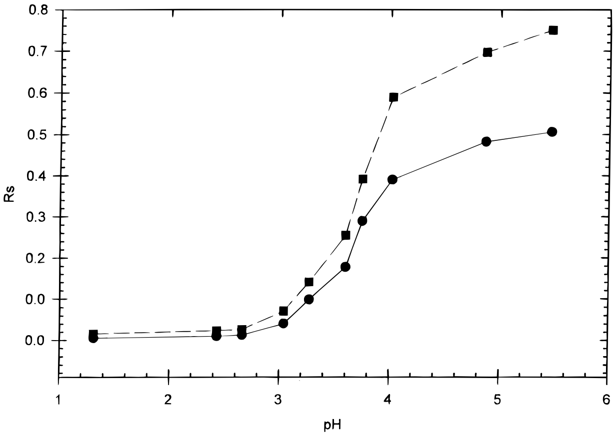

Figure 2. pH dependence of uranyl (10^{-4} M) sorption ratios (R_s) for control blank (solid line) and imprinted (dashed line) sol−gel glasses.

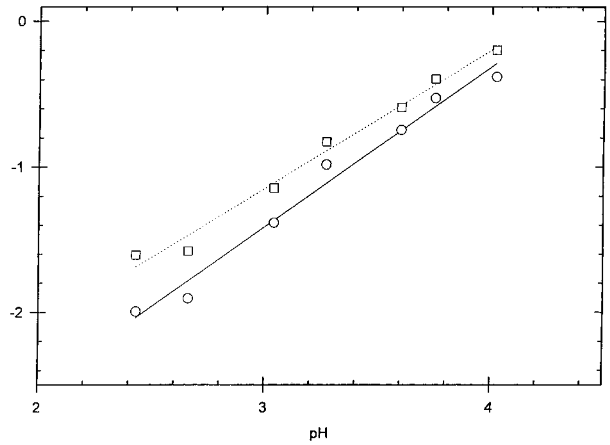

Figure 3. Plots of log(R_s) vs pH for control blank (dotted line) and imprinted (solid line) sol−gel glasses.

more uranyl-doped glasses, thereby eliminating secondary wastes from the imprinting process.

pH Dependence of Adsorption Capacity. As pointed out above, the adsorption capacity of silica materials toward uranyl ion is pH-dependent. Uranyl uptake from the solution was measured by the decrease of the total uranyl concentration in the solution as determined by the peroxide spectrophotometric method.[13] Figure 2 shows the plots of the sorption ratios (R_s's) of the control blank and the imprinted samples as a function of pH. The adsorption capacities of the imprinted glass are clearly larger than those of the control blank at all pH's investigated. The first term of the right side of eq 4 can be approximated as a constant[8b] at pH from 2.5 to 4.8 since the concentration of $\equiv$Si−OH in this pH range is usually quite large relative to [UO_2^{2+}]. The plots of log(R_s) vs pH (pH range 2.5−4.8) according to eq 4 are shown in Figure 3. The slopes (0.95 for the imprinted sample; 1.10 for the blank sample) of the two least squares lines fitted to the data are close to 1, consistent with eq 2. According to eq 4, the intersection value (log K') is proportional to the equilibrium constant (K) of eq 2. The intercept for the plot of the imprinted sample is −4.00, while that for the control blank is −4.71. The above analysis leads to the conclusion that the surface complexation of uranyl ion with the imprinted sample is stronger than that of the control blank sample.

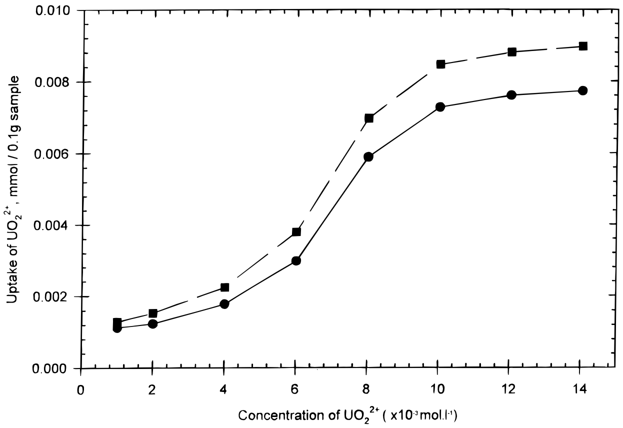

Figure 4. Uranyl-adsorption isotherms of control blank (solid line) and imprinted (dashed line) sol−gel glasses at pH = 5.06.

Adsorption Isotherm Studies. Adsorption isotherms for the sorbent samples were obtained by immersion in HOAc/NaOAc (0.26 M/0.54 M) buffer solutions (pH = 5.06) containing various concentration of uranyl ion (10^{-3}−10^{-2} M) for 24 h. The use of the above buffer solution was essential to keep the pH of solutions constant while the uranyl concentration was varied. Uranyl uptake from the solution was again measured by the decrease of the total uranyl concentration in the solution. Longer immersion times did not result in further increase of the uranyl uptake by either glass consistent with the attainment of equilibrium within the system. The use of buffered solutions ensures the same pH value for all samples, thereby resulting in the same surface charge of the sorbents. Accordingly, any adsorption differences can only be attributed to the uranyl adsorption equilibrium constants instead of changes in the surface charge. Figure 4 shows plots of the adsorption isotherms for blank and imprinted samples. The imprinted sample rebinds uranyl ion more strongly than the blank sample. The adsorption isotherms of both glasses cannot be described by Langmuir adsorption model (type I).[14] The general shapes are close to that of type V. Similar isotherms have been observed previously for the adsorption of inorganic cations by silica-based materials especially in equilibrium with high ionic strength solutions.[8c] The ionic strength of our uranyl solutions is also quite large because of the presence of the ionic buffer reagent (NaOAc). Accordingly, we tentatively attributed the type-V isotherm observed for our sol−gel sorbent materials to the high ionic strength in our uranyl solutions.

Adsorption Selectivity. The selectivities of the imprinted and control samples were evaluated by the competitive adsorption of uranyl ion on sol−gel glasses in the presence of excess cesium or calcium ions. The rationale for choosing Cs^+ as the competing ion is that Cs^+ is a fission product, which frequently coexists with uranyl ion in many radioactive waste samples. Calcium ion has the same formal charge as uranyl ion, and is frequently chosen as competing ions in testing selectiv-

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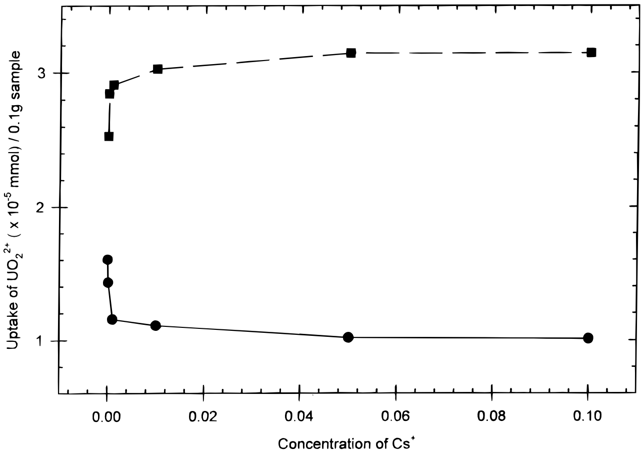

Figure 5. Plots of uranyl-adsorption capacities of control blank (solid line) and imprintd (dashed line) sol−gel glasses vs interfering Cs^+ concentration at pH 5.06.

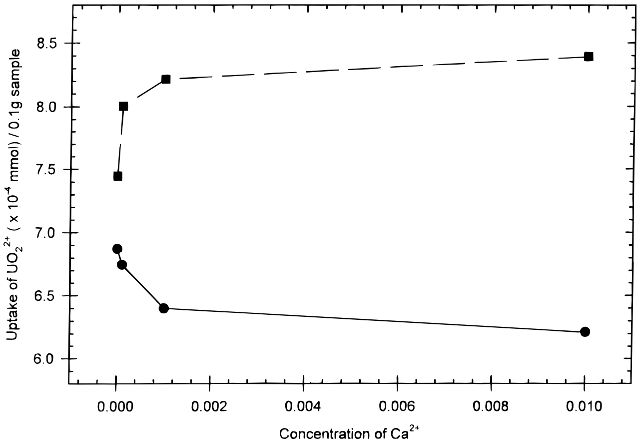

Figure 6. Plots of uranyl-adsorption capacities of control blank (solid line) and imprinted (dashed line) sol−gel glasses vs interfering Ca^{2+} concentration at pH 5.06.

ity of complexation ligands or sorbents.[15] The competition of $UO_2{}^{2+}$ with Cs^+ or Ca^{2+} for adsorption sites on the sol−gel glass surfaces is anticipated to lower the adsorption capacity of uranyl ion. Figure 5 shows the variation of adsorption capacity of imprinted and control blank samples with the concentration of cesium ion in the solutions, while Figure 6 gives the corresponding effect induced by the presence of Ca^{2+}. As seen in Figures 5 and 6, the capacity of the control blank sample decreases with the initial addition of Cs^+ or Ca^{2+}, whereas the opposite trend was observed for the imprinted glass. Surprisingly, the uranyl adsorption capacity of the imprinted glass is enhanced by the presence of Cs^+ or Ca^{2+}. While the decrease of the uranyl adsorption capacity of the control blank sample with Cs^+ or Ca^{2+} concentration is consistent with the competitive adsorption model, the increase of the adsorption capacity for the imprinted sample with Cs^+ or Ca^{2+} concentration is more difficult to rationalize. We tentatively attribute this phenomenon to a change in the activity coefficients (F term in eq 2) induced by the variation of the ionic strength in the solutions when Cs^+ or Ca^{2+} ions are present in solution. Similar phenomena have been observed for other systems.[8c] In the case of the control blank sample, the variation of the ionic strength is not enough to compensate for the competitive adsorption induced by added Cs^+ or Ca^{2+}.

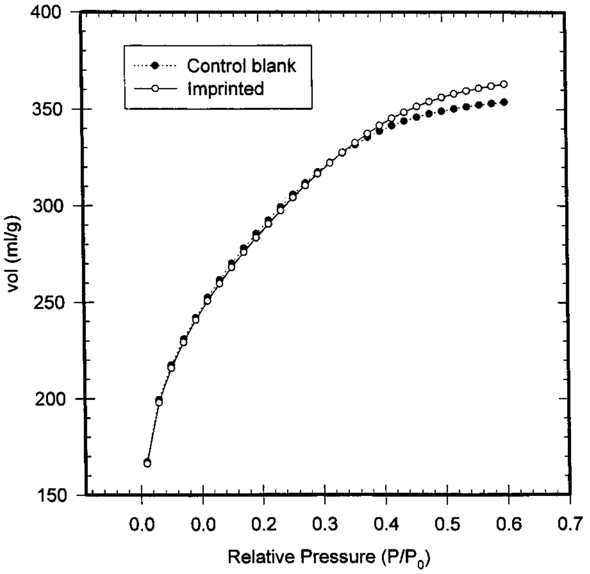

Figure 7. N_2-adsorption isotherms for control blank and imprinted sol−gel glasses.

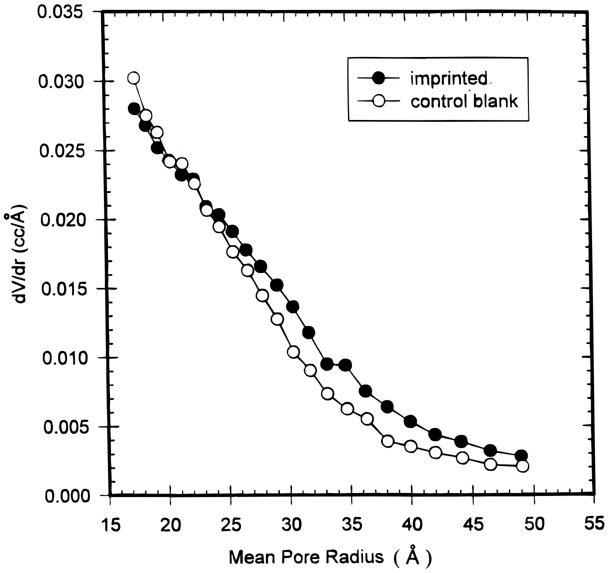

Figure 8. Pore-size distributions control blank and imprinted sol−gel glasses calculated via BJH method.

Surface Area and Pore-Size Distribution. Figure 7 shows the N_2-adsorption isotherms of the control blank and imprinted samples. Both isotherms can be reasonably well described by the Langmuir adsorption model (type I). This kind of the isotherm is typical for micro porous materials (pore size <20 Å) such as zeolites.[14] The BET surface areas of the two samples were found to be similar to one another: 999 m^2/g (blank) and 998 m^2/g (imprinted). Therefore, we cannot attribute differences observed for the uranyl adsorption capacity and selectivity observed for the imprinted and the blank samples to changes in overall surface area. Figure 8 shows the corresponding pore-size distributions from 17 to 50 Å calculated using the BJH (Barret−Joyner−Halenda) method.[16] This analysis indicates that there are negligible pores with sizes greater than

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50 Å. The lower limit (17 Å) is determined by our adsorption instrument and method. In general, the pore-size population increases inversely with the pore radius. This is consistent with the microporosity as inferred from adsorption isotherm measurements. In the mesoporous range (20−500 Å), little difference is observed in the pore-size distributions for two samples. Accordingly, imprinting the silica surface using a small template ion (diameter of UO_2^{2+} <10 Å) has little effect on the mesoporous structure of the final material. The microporous structure of the imprinted material may be quite different from that of the control blank. These micropores created by the imprinting process are considered to play key role for the enhanced adsorption capacity and selectivity of the imprinting sample. Experiments are currently underway to investigate the microporous structure of these materials.

Conclusions

Imprinting techniques have been applied to enhance the adsorption capacity and selectivity of sol−gel silica glasses toward uranyl ion. A significant increase in affinity and selectivity of the imprinted sol−gel sorbent over the control blank sample has been observed. Virtually no change in the surface area between the control blank and the imprinted samples was induced by the imprinting process. The enhanced capacity and selectivity are tentatively attributed to the change of the binding constant and the modification of the microporous structure induced by the imprinting technique.

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