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Synthesis and Characterization of Molecularly Imprinted Uranyl Ion Exchange Resins

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Abstract: Ion exchange resins with enhanced capacity and selectivity for UO_2^{2+} have been prepared using the molecular imprinting method. The imprinted structure was introduced by copolymerization of styrene with uranyl vinylbenzoate in the presence of divinylbenzene as the cross-linking agent. The polymerization was carried out in bulk with free-radical initiation using 2-methoxyethanol as a solvent and porogen. Upon removal of the template, specific sites for UO_2^{2+} rebinding remained. In equilibrium binding experiments with a variety of metal ions, the polymers preferentially bound UO_2^{2+}. Control experiments were performed with reference polymers prepared without the template (unimprinted) and Ni^{2+} imprinted polymers. Selectivity data show that the imprinted polymers have a higher affinity for UO_2^{2+} than any of the competing metal ions tested. Several variables, that are crucial in improving the capacity and selectivity of imprinted polymers, were investigated in detail. The variables included (1) the effects of template monomer content, (2) the degree of covalent cross-linking, and (3) the particle size. The effects of the variables on capacity and selectivity were examined and are discussed.

Keywords: Molecularly imprinted polymer, ion exchange, uranyl

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INTRODUCTION

Uranium poses health risks because of its toxicity, primarily to the kidneys, and is known to cause acute renal failure as well as delayed (several weeks or months) kidney problems (1). Uranium presents a radiological hazard because the metal and its decay products have been demonstrated to deposit in bones and cause cancer and birth defects (2). The major sources of uranium in the environment are industrial effluents and other wastes, primarily due to mining and weapons manufacturing. Uranium is present in seawater at trace concentration of (2.8–3.3 mg per liter) with other elements. The World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) set the limits of tolerable daily uranium intake at 0.6 μg/kg body weight. The maximum allowed concentration of uranium in drinking water is 20 μg per liter. In order to ensure that treatment of uranium waste does not lead to production of more waste, technologies that are capable of recovering uranium for reuse are needed.

The removal of ions such as uranyl by sorption into porous polymeric materials, namely ion exchange resins, is one of the most extensively used methods for the decontamination of various natural and industrial fluids and wastewater. However, the lack of selectivity and stability of the available chelating resins has made separation processes complicated (3). A different approach to the preparation of synthetic receptors such as ion selective exchange resins, is offered by the process of molecular imprinting (4–9). Molecular imprinting is a procedure with many attractive features and can be applied to a wide range of target molecules. In this technique, suitable polymerizable binding groups are linked to a template molecule that is copolymerized in the presence of a cross-linking agent to form cross-linked polymers. Removal of the template leaves binding sites possessing the shape corresponding to that of the template. The resulting polymer contains specific binding sites that recognize the imprint molecule and may exhibit a high selectivity for rebinding the template used in its preparation. The apparent simplicity and efficiency of molecular imprinting have made this technique increasingly popular in recent years, and several excellent reviews have been published (4). Molecularly imprinted polymers (MIPs) have been presented as artificial antibodies (10), catalysts (11), sensors (12), and as chromatographic stationary phases (13).

Although many successful applications of molecular imprinting in the separation of organic compounds have been reported (4), less attention has been paid to inorganic ions. The reports that have appeared in the literature concerning molecular imprinting for metal ions have dealt primarily with polymers prepared with Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Ca^{2+} and Zn^{2+}. The early reports were due to the groups of Kabanov (14) and Nishide (15). Subsequent reports on ion imprinted polymer resins have appeared using different methodologies (16–19). A few groups have specialized in the physical form of metal ion imprints and surface imprinting (20–22). Saunders et al. have shown that a 2-chloroacrylic acid/ethylene glycol dimethacrylate polymer can be imprinted for selective extraction of uranium (at $pH < 3$) (23). We reported an imprinted polymer membrane for the selective transport of uranyl ion (24). Say et al. have made imprints for uranyl ion using glutamic acid (25).

EXPERIMENTAL SECTION

Reagents

VBA was obtained from Sigma-Aldrich and recrystallized from ethanol. DVB, 2-methoxyethanol, and styrene were obtained from Sigma-Aldrich, 2,2′-azobisisobutyronitrile (AIBN) was obtained from Polysciences, Inc. (Warrington, PA) and were used as received. Standard solutions of uranyl nitrate were prepared from a 10,000 ppm stock solution (AA standard). Metal ion solutions for competitive rebinding studies were prepared from reagent grade solutions of nitrates and sulfates.

Instrumentation

A model 5400 ICP-MS (Hewlett-Packard) was used to verify metal ion concentrations in all sample solutions. Modulated Differential Scanning Calorimetry (MDSC) was performed using TA Instruments (New Castle, Delaware) Model DSC 2920 modulated differential scanning calorimeter. The pH was measured by employing a model 350 Corning pH/ionalyzer. FT-IR spectra were obtained using a Bomem Model MB-122 (Quebec, Canada). Electron micrographs were obtained using a Topcon Model DS-701 Scanning Electron Microscope (Pleasanton, California).

Preparation of Template Complexes

Uranyl vinylbenzoate was prepared by using 0.100 g (0.675 mmol) of vinylbenzoic acid (VBA) added to 0.5 mL ethanol and 2.0 mL water. A few drops of 0.1 M NaOH were added to aid dissolution and to make the solution slightly basic. Then 2.0 mL of 0.168 M uranyl ion solution in 1% nitric acid was added to the VBA solution, which immediately precipitated the uranyl vinylbenzoate salt. The mixture was made neutral, again by the addition of 0.1 M NaOH and was heated to 60°C and stirred for 30 min. The yellow salt was filtered, washed with hot water, and dried. The yield of the template complex was 88%. A second reaction doubled the amount of reactants under the same conditions and produced a 97% yield; IR (KBr, cm^{-1}) 3400 (b, H_2O); 1680 (C═C vinyl stretch), 1605 (C═C ring stretch); 1550 (C═O carboxylate stretch, symmetric); 1300 (C–O stretch); 1200 (C–O stretch); 990 (C═C–H stretch); 920 (UO_2^{2+} anti-ion symmetric vibration); 860 (UO_2^{2+} ion symmetric vibration). Melting point (MP), 225°C. Elemental analysis (ICP-MS): $UO_2(VBA)_2 \bullet H_2O$, U 40.7%, calc.40.9%. Nickel vinylbenzoate complex was prepared by a procedure already reported (26); yield, 85%. Elemental analysis (ICP-MS), $Ni(VBA)_2 \bullet 3H_2O$, Ni 14.2%, calculated 14.4%.

Polymer Preparation

Uranyl vinylbenzoate (1–5 mol% with respect to total monomer) dissolved in 2-methoxyethanol (0.4 mL) was added to a screw cap vial containing styrene and sonicated for 5 min. The solution was then purged with nitrogen for 5 min. DVB (1.0–80 mol % with respect to total monomer) and AIBN (1.0 mol% with respect to total monomer) were added to the mixture. The mixture was again purged with nitrogen. The polymerization reaction was carried out at 60°C for 24 h under a nitrogen atmosphere in an ultrasonic bath. Nickel imprinted and blank (unimprinted) polymers were prepared in the same manner to serve as reference. Bulk polymers were ground into powder with a cryogenic ball mill (Spex Industries). The ground polymers were washed with acetone, then acetone and water with increasingly larger amounts of water until only water was used. This procedure removed unreacted monomers and served to swell the polymers. Once cleaned, the resins were allowed to dry overnight in ambient air. Subsequently, they were washed with 1 M HNO_3 until the wash solution was free of metal ions as verified by ICP-MS. The polymers were rinsed with deionized water until the wash water tested neutral to pH paper and were again allowed to dry overnight in ambient air. The imprinted resins were deemed ready for use in the loading and selectivity studies.

Capacity Measurements

To determine the rebinding characteristics of the imprinted polymers, previously cleaned resins were loaded with uranyl ions in batch mode equilibrations. The resins (50 mg) were placed in a plastic container (30 mL), to which was added 4.2×10^{-4} M uranyl nitrate solution (20 mL). The metal ion concentration was selected by referring to the speciation conditions of uranyl ion (27). The pH of each mixture was adjusted by addition of dilute HNO_3 or NaOH to the value required for each experiment. The mixture was shaken during equilibration at 30°C for 24 h. The equilibrated mixture was filtered and washed with deionized water to remove metal ions not specifically bound to the resin. The resins were washed until the wash solution was neutral to pH paper and left to air dry for 24 h. After drying, samples loaded with uranyl ions were weighed into plastic bottles and combined with water. The pH of each mixture was adjusted to 2.6–2.7 by the addition of dilute nitric acid and equilibrated overnight with gentle stirring in a controlled temperature chamber maintained at 30°C. After equilibration, an aliquot was removed from the mixture; the pH recorded and analyzed for metal ion concentration. The resins were further equilibrated with nitric acid at pH 1. After a second overnight equilibration period, the solution was again analyzed for metal. Resins were reused after water washing. Repeated extraction without loading indicated that all available metal ions were removed by this procedure as determined by ICP-MS. The capacity of the polymer was equivalent to the amount of metal ions removed from the polymer in both parts of each extraction.

The data acquired from the procedure described above were used in the following equations to calculate the metal ion capacity and the equilibrium constant:

$$\mathrm{Capacity} = \frac{[\mathrm{M}^{2+}]_1\mathrm{V}_1 + [\mathrm{M}^{2+}]_2\mathrm{V}_2}{\mathrm{W}_1} \tag{1}$$

where W_1 is the amount of dry polymer weighed into the vial; $[M^{2+}]_1$, $[M^{2+}]_2$ are the concentrations of the metal ion in the solutions for the first and second overnight equilibrations, V_1, V_2 are the volumes the solution removed after first overnight extraction and the solution for second overnight extraction, respectively.

The adsorption of a metal ion M^{2+} by a ligand R can be formulated in terms of the following cation-exchange equilibrium:

$$\mathrm{M}^{2+} + 2\mathrm{HR} \leftrightarrow \mathrm{MR}_2 + 2\mathrm{H}^+ \tag{2}$$

where R represents the resin. At equilibrium, the equilibrium constant is:

$$\mathrm{K} = \frac{[\mathrm{H}^+]^2[\mathrm{MR}_2]}{[\mathrm{M}^{2+}][\mathrm{HR}]^2} \tag{3}$$

and

$$\mathrm{K} = \frac{[\mathrm{H}^+]^2(\mathrm{Capacity} - [\mathrm{M}^{2+}]\mathrm{V}_1/\mathrm{W}_1)}{[\mathrm{M}^{2+}](2[\mathrm{M}^{2+}]\mathrm{V}_1/\mathrm{W1})^2} \tag{4}$$

where V_1 is the volume of the solution for first overnight extraction, $[H^+]$ is the concentration of hydrogen ions in the water phase at equilibrium, $[MR_2]$ is concentration of metal ions in the polymer phase, [HR] is the hydrogen ion concentration in the polymer phase, and $[M^{2+}]$ is the concentration of metal ions in the water phase at equilibrium.

Selectivity

The polymers (typically 50 mg) were treated with an equimolar mixture (4.2×10^{-4} M) of a solution containing both metal ions (UO_2^{2+}, M^{n+}). After equilibration in the manner described above, the polymers were filtered and washed with deionized water. The analytes were recovered by washing with nitric acid and analyzed for metal ions. The selectivity values were determined according to the following equation:

$$\alpha_{UO_2^{2+},M^{2+}} = \frac{\text{Capacity } UO_2^{2+}}{\text{Capacity } M^{n+}} \tag{5}$$

RESULTS AND DISCUSSION

Synthesis and Characterization of Imprinted Polymers

The bulk polymers ranged from bubbly yellow-brown solids (uranyl imprinted polymers) to bubbly dark green solids (nickel imprinted polymers). The ground polymers were sieved into fractions of differing size. Approximately 64% of the theoretical amount of the template ion was extracted by washing with 1 M HNO_3 for 36 h. (Additional recovery occurs upon prolonged sonication adding up to a value of approximately 91%.) The theoretical recovery is calculated based on the weight of template per total weight of monomers in the initial mixture (DVB, styrene, and template complex). Scanning electron microscopy (SEM) was used to image the resins (Fig. 1). The surface of the resins is shown to be porous at high magnification.

Figure 2 shows the trend in the glass transition temperature (T_g) for a series of polymers containing a fixed level of covalent cross-linking (2 mol%) with varying template complex monomer. The values were

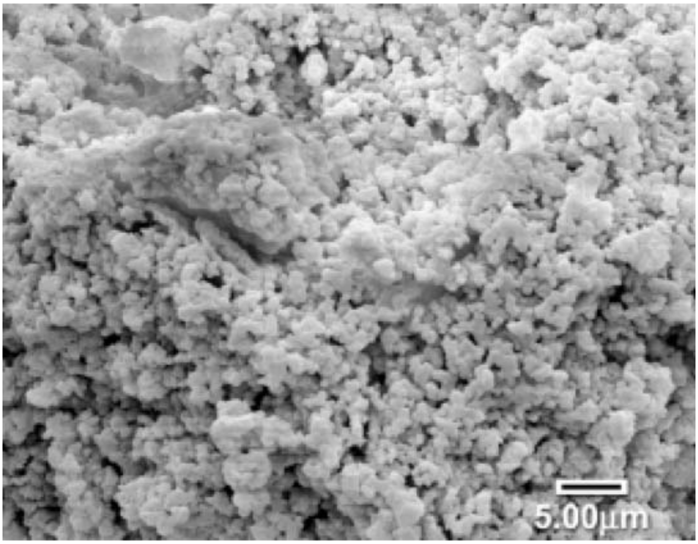

Figure 1. Scanning electron micrograph of the surface of uranyl imprinted polymer.

obtained by using Modulated Differential Scanning Calorimetry (MDSC). The linear dependence of T_g toward covalent cross-linking is well understood. The dependence of T_g on metal ion cross-links is more complex. The theory describing the effects of metal ion cross-linking is reviewed by Eisenberg and Kim (28). In their theory, as the amount of metal ion content increases, metal ion aggregation occurs. This aggregation is due to the low dielectric constant of the bulk polymer. When aggregation occurs there is a large increase in the rigidity of the polymer in the area of the aggregation. This is often seen as a sharp increase in the bulk Tg as measured by MDSC or as a new high-temperature T_g when using Dynamic Mechanical Analysis (DMA). A sharp increase is observed when the template monomer is increased from 4 to 5 mol%. Since extraction of the template ion is incomplete, the effect on the polymer T_g is probably due to residual metal ion cross-links. The presence of residual metal ion cross-links may have a significant effect on exchange selectivity and help explain why metal ion exchange resins with relatively low amounts of covalent cross-linking still maintain a high selectivity and stability. DMA data obtained for Pb^{2+} imprinted polymers showed that two Tg's were found when metal complex content reached 4% (29).

Rebinding Studies

Cation-exchangers with weak exchange site such as carboxylic acid resins require moderately high pH values for effective exchange. Solution pH has

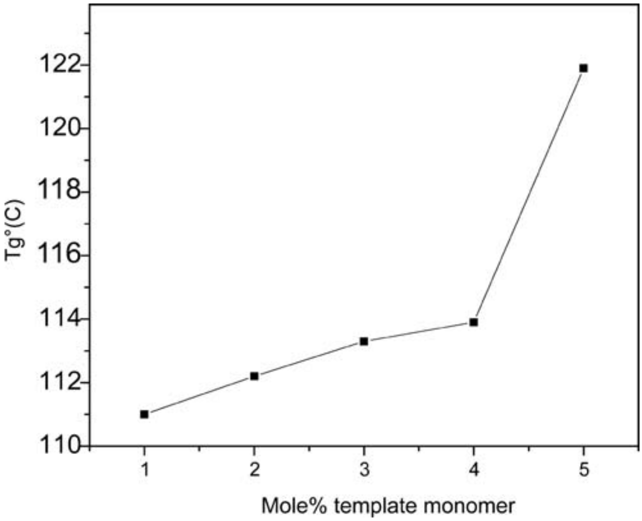

Figure 2. The glass transition temperature of polymers with increasing template monomer.

two kinds of influence on metal sorption: (1) an effect on the solubility and speciation of metal ions in solution, and (2) an effect on the overall charge of the sorbent. UO_2^{2+} is easily hydrolyzed into various forms as described by Baes and Mesmer (27). In these studies, the pH was set to either 3.5 or 5.3, by adjustment with dilute HCl or NaOH.

Influence of the Resin Particle Size on the Capacity

The ground polymers were sieved into five different fractions of mesh size (US Standard) 20, 40, 60, 80, and 100, with particle diameters of 0.850, 0.425, 0.250, 0.180, and 0.150 mm, respectively. Samples of each size were loaded with uranyl ions and the capacity was determined. The influence of particle size on the exchange capacity can be seen in Fig. 3. The capacity increases gradually for particles with diameter 0.85 to 0.18 mm. A sharp increase in capacity is observed as the particle diameter decreases from 0.18 to 0.15 mm. The last fraction contains polymer particles with diameters 0.15 mm and smaller in a range of 0.15–0.053 mm, resulting in the anomalous increase. Still, it appears that the particle size has a contribution to exchange capacity in excess of that expected by a linear increase in surface area. Ion sorption into ion-exchange solids involves the diffusion of ions from the solution to the resin surface and the diffusion of ions within the solid resin (30). Since some of the metal could not be removed from the

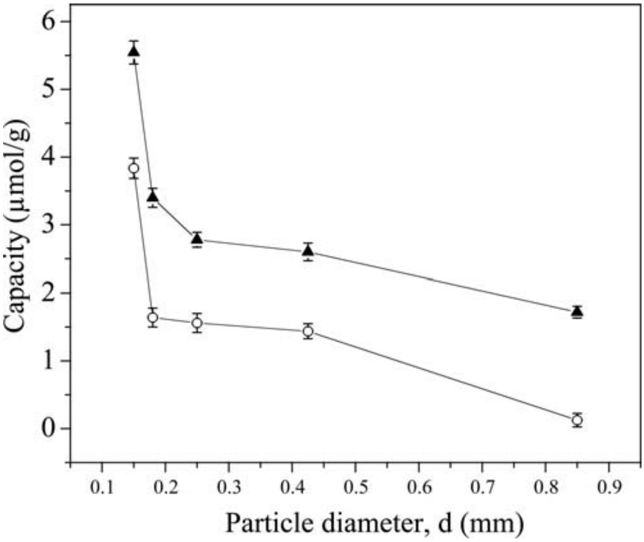

Figure 3. The influence of particle size on the capacity of the imprinted resins with (▲) 5 mol% template monomer and 2 mol% cross-linker; (○) 2 mol% template monomer and 3.5 mol% cross-linker at pH 5.3.

resins it is reasonable to suspect that facile exchange is restricted to a certain depth indicating a surface volume for exchange.

A model that includes a reasonably constant depth of exchange appears to better fit the experimental data. The method assumes that the template complex used in the copolymerization is homogeneously dispersed in the bulk polymer. A set of equations was used for the calculation.

$$V = \frac{4}{3}\pi r^3 \tag{6}$$

$$dV = 4\pi r^2 dr \tag{7}$$

$$\frac{dV}{V} = 3\frac{dr}{r} \tag{8}$$

The calculation assigns the measured capacity to the volume accessible to exchange (dV) and the theoretical capacity to the total volume (V). Using these assignments, the depth (dr) associated with the effective exchange volume is calculated. The experimental value for the capacity of the 5 mol% resin (100 mesh) is 5.54 μmol/g. The amount of complex loading based on the polymer feed is 384.56 μmol/g. The volume of 100 mesh beads ($r = 7.5 \times 10^{-3}$ cm) is 1.8×10^{-6} cm^3. The portion of the surface volume equal to the experimental exchange capacity yields an active surface depth of about 3.6×10^{-5} cm or 360 nm. A much larger polymer bead, 40 mesh ($r = 2.12 \times 10^{-2}$ cm), whose experimental capacity is 2.61 μmol/g when subjected to the same calculations, the active surface depth was found to be 4.79×10^{-5} cm or 479 nm. The penetration depth (dr) was set constant at an average value of 4.1×10^{-5} cm. From Eq. (8)

$$\mathrm{dV/V = 3dr/r = dCap/Cap} \tag{9}$$

$$\mathrm{dCap = 6dr/d} \tag{10}$$

where d is the diameter of the particle. From these expressions the theoretical capacity dCap was calculated using the following expression:

$$\mathrm{dCap = (6dr/d) \times Cap \quad (Cap = 384.mol/gram)} \tag{11}$$

A graph of this theoretical capacity is given as Fig. 4.

Influence of Template Monomer Loading on the Metal Ion Capacity

Figure 5 shows the influence of template monomer (uranyl vinylbenzoate) loading in the polymerization mixture for a series of polymers of constant cross-linking (1 and 2 mol% DVB). The studies were conducted at pH 3.5 and 5.3. As expected, exchange capacity increases with template loading and the capacity is higher at pH 5.3 than at pH 3.5. The equilibrium constants of the polymers are presented in Table 1 and are calculated from

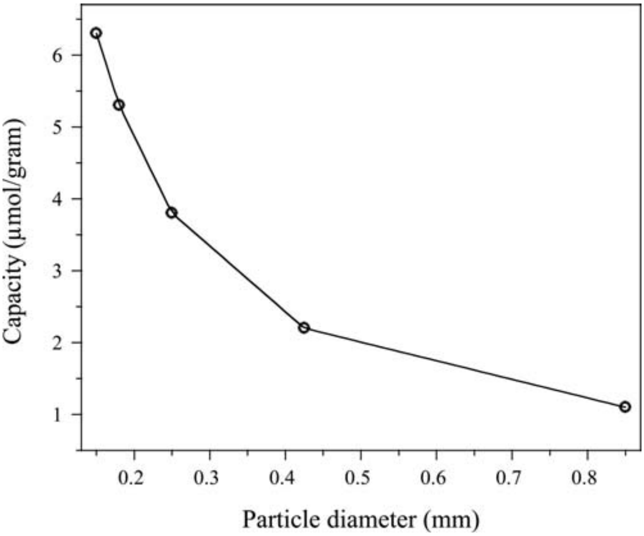

Figure 4. Variation of theoretical capacity with particle diameter.

Eq 4. These constants were determined by the acid and metal ion concentration in the aqueous phase and in the polymer phase. The [H^+] in the water phase was computed from the pH of the solution and the metal ion concentration was determined by ICP-MS. The concentration of metal ions in the polymer phase was calculated as the difference between the capacity of the

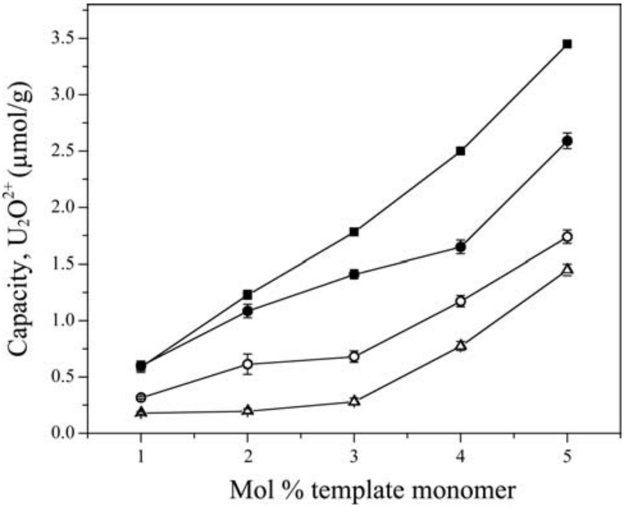

Figure 5. The effect of the imprint complex loading on the capacity of polymers with 1 mol% DVB at pH 3.5 (○) and 5.3 (■); 2 mol% DVB at pH 3.5 (△) and pH 5.3 (●).

Table 1. Effect of template monomer loading on equilibrium constant

Template complex (Mol%)	Cross-linker (DVB) (Mol%)	Log K
1.5	1	5.09 ± 0.07
3	1	4.86 ± 0.09
4	1	4.59 ± 0.06
5	1	2.54 ± 0.02
3	2	6.56 ± 0.33
4	2	5.74 ± 0.37

polymer and the amount of the metal ion that was exchanged into solution at equilibrium, divided by the weight of the resins. The hydrogen ion concentration in the polymer phase was calculated as twice the amount of uranyl ion in solution at equilibrium divided by the weight of resins used. Unlike the capacity values, the equilibrium constants decrease as template content increases. The trend has also been reported and explained for Ni^{2+}, Cu^{2+}, and Pb^{2+} imprinted polymers (18, 19).

Influence of the Degree of Cross-linking on the Capacity

A series of polymers of varying level of covalent cross-linking were synthesized in the presence of a constant amount of template monomer in the polymerization mixture (1 mol%) to ascertain the effect of the degree of covalent cross-linking on the rebinding capacity. The affinity of the cross-linked polymers toward UO_2^{2+} is illustrated in Fig. 6. The capacity decreases as covalent cross-linking increases from 1–6 mol% DVB. The decrease in capacity is explained by rigidity and reduced access to binding sites deep in the resin particles (31, 32). In comparison, polymers prepared with high complex content and much higher amounts of covalent cross-linker (5 mol% complex, 80 mol% cross-linker) showed higher rebinding capacities of 5.9 ± 0.2 and 10.6 ± 0.15 μmol/g at pH 3.5 and 5.3, respectively, but reduced selectivity. The higher capacities are a result of the macro-porosity of the polymer with this level of covalent cross-linking compared to those with low levels of covalent cross-linkers. The macroporous structure allows more sites to be accessible for rebinding of the metal ions and reduces the amount of residual metal ion cross-links.

Effect of Imprinting on the Capacity

In order to examine the affinity arising from the imprinting effect, the metal adsorption behavior of the imprinted, blank, and Ni^{2+} imprinted polymer

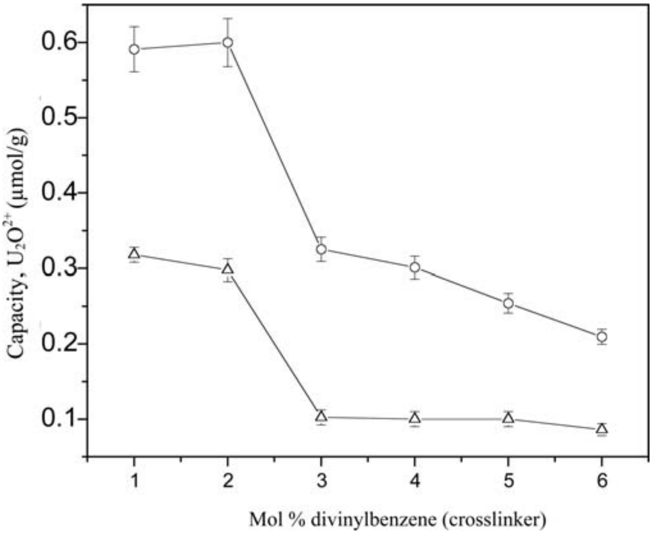

Figure 6. The effect of cross-linking on the capacity of imprinted polymers with 1.0 mol% template monomer at pH 3.5 (Δ), and 5.3, (O).

resins were examined. The rebinding capacities of the resins made using 2 mol% complex and 2 mol% cross-linker are shown in Table 2. Comparison of the values in Table 2 show that UO_2^{2+} is more effectively absorbed by the uranyl ion imprinted polymer resin than by the blank or nickel imprinted polymers. The low adsorption of UO_2^{2+} on the Ni^{2+}-imprinted polymer resin reveals that metal ion occupancy does not act merely as a spacer to allow metal ion access. The rebinding affinities of the imprinted and unimprinted polymers of constant cross-linking (2 mol%) were investigated to evaluate the trend in the rebinding capacity. Figure 7 shows the adsorption behavior of the imprinted polymers compared to that of the unimprinted polymers. The capacity of the imprinted polymers was found to be 8 to 10 times higher than that of the blank polymers. The affinity of the unimprinted polymer for ions is used to obtain corrected selectivity values.

Table 2. Comparison of the rebinding capacity of resins imprinted with UO_2^{2+}, Ni^{2+} and blank (random) resins. All polymers were 2 mol% template monomer and 2 mol% cross-linker

Polymer type	Capacity (μmol/g), pH 3.5	Capacity (μmol/g), pH 5.3
Ni-imprinted	0.058 ± 0.004	0.321 ± 0.007
UO_2^{2+} imprinted	0.407 ± 0.002	1.09 ± 0.02
Blank (random)	0.021 ± 0.005	0.102 ± 0.003

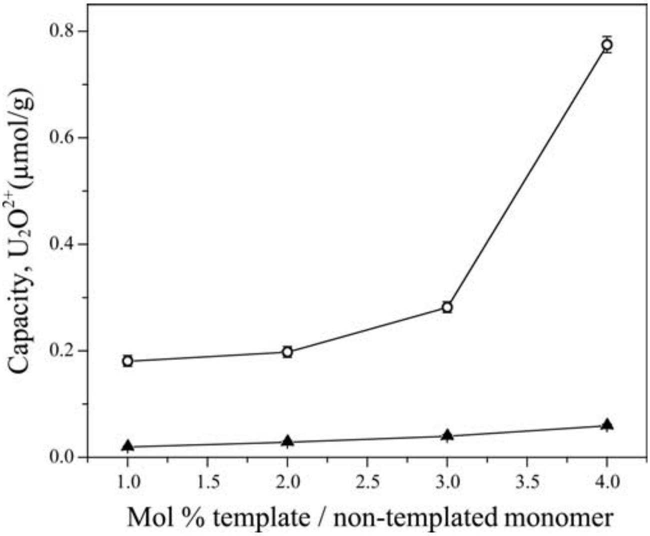

Figure 7. Capacity of imprinted (▲) and unimprinted polymer (○) containing 2 mol% DVB as cross-linker at pH 3.5.

Selectivity and the Role of Cross-linker

Selectivity was evaluated by multiple ion exposure experiments. The results of the studies on the selectivity of the polymer resins toward Ni^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+} in competitive rebinding are summarized in Table 3. In all cases, the resins were selective toward uranyl ion. The degree of cross-linking contributes to selectivity as well as the rebinding capacity. The results of the investigation of the dependence of selectivity on the degree of cross-linking are summarized in Table 4. Selectivity is shown to decrease as the cross-linker is increased from 1 to 5 mol%. This trend mirrors the observed decrease in capacity with increase in cross-linking discussed earlier, for the same polymers

Table 3. Selectivity of uranyl ion imprinted polymer resins in multiple exposures (pH 3.5). Solution contains 4.2×10^{-4} M of UO_2^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+}

Template monomer (mol%)	Cross-linker (DVB) mol%	αUO_2^{2+}, Ni^{2+}	αUO_2^{2+}, Cd^{2+}	αUO_2^{2+}, Cu^{2+}	αUO_2^{2+}, Fe^{3+}
2	1	7.02 ± 0.49	9.11 ± 0.46	9.12 ± 0.15	4.3 ± 0.29
3	2	9.91 ± 0.28	7.27 ± 0.35	12.7 ± 0.4	6.12 ± 0.17
5	2	9.24 ± 0.11		9.72 ± 0.14	8.4 ± 0.33
5	3	11.6 ± 0.2		12.3 ± 0.2	10.6 ± 0.1

Table 4. Effect of cross-linker on the selectivity of a polymer containing 1.0 mol% template monomer (pH 5.3). Solutions contained 4.2×10^{-4} M of UO_2^{2+} and Cd^{2+}

Cross-linker (mol%)	Selectivity, α, UO_2^{2+}, Cd^{2+}
1	9.78 ± 0.49
2	7.98 ± 0.39
4	6.58 ± 0.33
5	5.74 ± 0.26

The blank resins should exhibit a certain degree of metal-ion selectivity, owing to the different strengths of interaction of the metal ions with the randomly distributed binding groups. Experiments with the unimprinted polymers show that they bind nearly equal amounts UO_2^{2+} and the competing metal ions. In contrast, polymers prepared in the presence of UO_2^{2+} as a template exhibited substantial preferences for UO_2^{2+} in both saturation and competitive rebinding experiments. A comparison of the selectivity (α) values of the imprinted resins with those of the blank resins is a better measure (α') of the effect of imprinting on selectivity. As a measure of imprinting efficiency, we define a relative selectivity α' as follows:

$$\alpha' = \frac{\text{Selectivity of the Imprinted Polymer}}{\text{Selectivity of the Unimprinted Polymer}} \tag{12}$$

Where the unimprinted polymer is prepared without the template. The summary of the results showing the efficiency of imprinting on selectivity is shown in Table 5. The selectivity ratio α of polymers with 2 mol% cross-linker and variable template complex content are compared to the selectivity of blank polymers of corresponding composition but unimprinted. The ratio is high indicating clearly that molecular imprinting of UO_2^{2+} has enhanced the selectivity.

Reproducibility

In order to make inferences from trends, the reproducibility of the data must be known. Table 6 shows the values of capacity and percent relative standard deviation (%RSD) obtained in replicate measurements at pH 3.5 of different samples of resins from the same batch. Resins of different batch (resins of the same composition prepared separately, batch-to-batch preparation) show capacity with an RSD between 5–11% based on a three-batch preparation of polymer resins containing 1 mol% complex and 2 mol% cross-linker (RSD = 5%), 2 mol% complex and 2 mol% cross-linker (RSD = 7%), 2 mol% complex and 1 mol% cross-linker (RSD = 11%). Since the sample

Table 5. Effect of imprinting (α') on selectivity for polymers containing 2 mol% cross-linker and variable template monomer (pH 3.5)

Template monomer (mol%)	Cross-linker (mol%)	$\alpha'UO_2^{2+}$, Cd^{2+}	$\alpha'UO_2^{2+}$, Cu^{2+}	$\alpha'UO_2^{2+}$, Ni^{2+}
1	2	19.05 ± 0.38	10.1 ± 0.2	24.5 ± 0.4
2	2	21.4 ± 0.53	15.6 ± 0.4	29.5 ± 0.3
3	2	33.0 ± 0.9	21.4 ± 0.3	33.5 ± 0.9
4	2	37.2 ± 1.3	23.2 ± 0.5	36.2 ± 1.4

to sample variability of the same batch is of the same order of magnitude as the batch to batch variability, we feel that the trends we have observed are valid.

CONCLUSIONS

Uranyl ion imprinted polymers prepared have improved binding characteristics as observed in their higher capacity and selectivity compared to unimprinted polymers. Several factors may be responsible for the properties of the imprinted polymers. The role of the cavity size is apparent when uranyl ion binding in UO_2^{2+} and Ni^{2+} ion imprinted polymers were compared. The results showed low binding of uranyl ion to the nickel-imprinted polymer. This suggests that the cavity left by nickel imprinting could not sufficiently accommodate uranyl ion. It also shows that the size of the cavity and the orientation of the functional groups inside the cavity contribute to molecular recognition.

The dimensional stability and matrix rigidity leading to the preservation of the spatial arrangement of the metal ion coordinators require the use of a

Table 6. Capacity and percent relative standard deviation (% RSD)[a]

Polymer ID	Template (mol%)	Cross-linker (mol%)	Number of measurements (n)	Capacity (mean) μmol/g	%RSD[b]
P12	1	2	4	0.18	7.33
P22	2	2	4	0.21	9.29
P32	3	2	6	0.29	5.91
P42	4	2	4	0.78	4.15
P52	5	2	4	1.66	2.23

[a] Replicate measurements using resins of the same batch. All resins were used once and stored.

[b] %RSD calculated as (s/m) × 100, where s = standard deviation and m = mean.

cross-linking agent. A high degree of cross-linking adversely effects selectivity. For reversible binding, and increased rebinding kinetics, the flexibility of the polymers plays a significant role. Therefore, a compromise must be found between a rigid arrangement of the polymer chains to give high selectivity and an appropriate degree of flexibility that is necessary for good accessibility of the cavities and rapid attainment of binding equilibrium. The combination of these properties, the simplicity of the system, and its excellent performance should be advantageous for a number of applications. Based on the results presented, MIP's promises to be a useful tool for the selective extraction and clean up of target molecules from complex environmental samples.

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