Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 08 November 2003

To cite this Article Say, Rıdvan , Ersöz, Arzu and Denizli, Adil(2003) 'Selective Separation of Uranium Containing Glutamic Acid Molecular-Imprinted Polymeric Microbeads', Separation Science and Technology, 38: 14, 3431 — 3447
To link to this Article: DOI: 10.1081/SS-120023407
URL: http://dx.doi.org/10.1081/SS-120023407

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 14, pp. 3431–3447, 2003

Selective Separation of Uranium Containing Glutamic Acid Molecular-Imprinted Polymeric Microbeads

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INTRODUCTION

Uranium, which is included in lanthanides series and an element with the highest atomic number of any naturally occuring element, is found in granites, metamorphic rocks, lignite, monazite sands, and phosphate deposits as well as minerals. The concentration in phosphate rocks can be as high as 0.12 mg/g.[1] Currently, uranium is the most important nuclear fuel. Enriched uranium is used as a material of high density in the aeronautics industry, as radiation shielding, as an additive for catalysts or steels, and in the glass and ceramics industries. Some plants, such as olive trees and certain fungi, are able to store uranium contents of several g/kg.[2] Uranium compounds are extremely

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DOI: 10.1081/SS-120023407 0149-6395 (Print); 1520-5754 (Online)

poisonous and cause kidney and liver damage. The most stable form of uranium that probably exists in most of the body fluids is dioxouranium(VI), commonly known as the uranyl ion. This is an ion of intermediate hardness with high affinity for carboxylate functional groups, although it has been reported that substituted catechols are also good ligands. The removal of uranium from the body has been studied by a number of investigators.[3] Mostly, the low concentrations of uranium encountered and the presence of high levels of interfering matrix constituents prevent its direct determination. Because of this, various separation and preconcentration techniques are employed for the determination of uranium. Although liquid–liquid extraction has been widely used,[4] it is time consuming. Extraction chromatography,[4,5] solid-phase extraction,[1,6,7] supercritical fluid extraction,[8] ion exchange,[9] and adsorbents[10,11] have been extensively used for the separation and preconcentration of uranium ions. The process of using adsorbents is an effective method for heavy metals by using metal chelating resins prepared with containing aminoacid monomer ligands[12–14] and for recovering uranium because of the high selectivity for uranium, the ease of handling, and environmental safety. The solid-phase extraction methods using molecular imprinted polymers are the most used methods for the separation and preconcentration of trace metals.[15–17] Molecular imprinting is a method for making selective binding sites in synthetic polymers by using molecular template. Metal cations can be used as templates for imprinting crosslinked polymers. After the removal of template (the cation), the remaining polymer is more selective. The selectivity of the polymer depends on various factors, like the charge on the cation, the size of the cation, the specificity of the interaction of the ligand, the coordination geometry, and the number of the cations. Transition metals can also be removed by using the molecular imprinting method.[18–20] During the imprinting procedure, metal coordination is also used in many cases. Molecularly imprinted polymers prepared with metal-chelate monomers have been used to examine the roles of metal ion and ligand shape on binding selectivity.[21–23]

The imprinted polymer has greater selectivity for the uranyl ion than does either the monomer ionophore or nonimprinted polymers.[23,24] In this study, an ion-imprinting polymer prepared with methacryloylamidoglutamic acid (MAGA) was used for selective separation of uranyl ions from aqueous solutions. Glutamic acid was chosen because glutamic acid molecules are linked to the backbone through primary amine groups and the pendant carboxyl groups are responsible for the uranium binding. Strong complex formation occurs between carboxylic groups and uranyl ions.[25] We selected MAGA as the metal complexing monomer by template polymerization, with the goal of preparing a solid-phase that has high selectivity for uranyl ions.

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P(MAGA-UO_2^{2+}-co-EGDMA) metal complexing microbeads were produced by a dispersion polymerization technique. After removal of UO_2^{2+} ions, uranyl adsorption on the UO_2^{2+} ion-imprinting microbeads from aqueous solutions containing their different amounts, at different pHs, selectivity study of uranyl vs other interfering metal ions mixture, which are Fe^{3+}, Mn^{2+}, and Th^{4+}, and distribution and selectivity coefficients are reported here. Finally, repeated use of the UO_2^{2+}-imprinted polymeric microbeads from water is also discussed.

EXPERIMENTAL

Materials

Glutamic acid and methacryloylchloride were supplied by Sigma (St. Louis, MO) and uranyl nitrate.hexahydrate and thorium nitrate.hydrate by Fluka and used as received. Ethyleneglycoldimethacrylate (EGDMA) was obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor, and stored at 4 °C until use. Azobisisobutyronitrile (AIBN) was also obtained from Fluka (Switzerland). Poly(vinylalcohol) (PVAL; MW: 10.000, 98% hydrolyzed), dibenzoylmethane (DBM), and Lawsone were supplied from Aldrich Chemical (USA). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the experiments was purified using a Barnstead (Dubuque, IA) ROpure LP reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANO pure organic/colloid removal and ion exchange packed-bed system.

Instrumentation

A Shimadzu UV-2101 PC UV-VIS scanning spectrophotometer and 10-mm quartz cells were used for spectral measurements. Colorimetric methods for uranium are relatively sensitive. Several extraction methods exist for the determination of very small amounts of uranium in aqueous samples. DBM is one of the colorimetric reagents used for the determination of uranium in aqueous solutions. For the colorimetric determination of UO_2^{2+} by DBM, 28 mL of 95% ethyl alcohol was added to 10 mL of slightly acidic test solution containing 2 to 10 ppm U(VI). The total volume was then brought 40 mL with dionized water. The pH was adjusted to 2 to 3, and exactly 1 mL of 1% DBM

in ethyl alcohol solution was added to the solution. After mixing, the pH of the resulting solution was brought to between 7.5 and 8.0 to develop the color and then diluted. The absorbance of uranium-DBM complex solution was monitored at 405 nm against a reagent blank in ethyl alcohol.[23,26]

Atomic absorption spectral measurements were performed in Carl Zeiss Technology AAS 5EA atomic absorption spectrophotometer (AAS) pyrolytically coated HGA-76 graphite furnace (GF). An uranium hollow cathode lamp was used at 358.5 nm uranium wavelength with a spectral width of 0.2 nm. The atomization temperature of 2650°C and argon gas purge was used.[27] A Fisher Scientific, Accumet Basic AB15 pH-meter was used to measure pH values.

Synthesis of 2-Methacryloylamidoglutamic Acid (MAGA) Monomer

For synthesis of MAGA monomer, the following experimental procedure was applied: 5.0 g of glutamic acid and 0.2 g of hydroquinone were dissolved in 100 mL of CH_2Cl_2. This solution was cooled down to 0°C. Thirteen g of triethylamine was added into this solution, then methacryloylchloride was poured slowly into this solution. The resulting solution was stirred under nitrogen atmosphere magnetically at room temperature for 3 h. At the end of chemical rection period, the unreacted methacryloylchloride was extracted with 10% NaOH solution. The aqueous phase was dried with $MgSO_4$ and evaporated in a rotary evaporator. The residue was crystallized in ethanol and ethylacetate. [Yield 73.7 %; 1H-NMR ($CHCl_3$): δ 1.19 to 1.23 (m; 2H, CH_2), 1.50 to 1.55 (m; 2H, CH_2), 1.90 (s; 3H, CH_3) 4.49 to 4.59 (m; 1H, CNH), 5.33 (s; 1H, COH_2), 5.73 (s; 1H, COH_2), 6.87 (δ; 1H, NH), 9.58 (δ; s, 2H, COOH). FTIR (KBr, cm^{-1}):$\nu = 3626$ (alcohol vibration band with hydrogen bonding); 1732 (ester band); 1655 (carbonyl band); 1640 (amide I band); 1548 (amide II stretching vibration band); 1490 (amide II vibration band); 1300 and (C—O stretching band).]

Synthesis of the Uranyl-methacryloylamidoglutamic Acid Monomer

MAGA (0.215 g, 1.0 mmol) was added slowly into 15 mL of ethanol and uranyl nitrate (1.0 mmol) at room temperature to this solution with continuous stirring. The solution was allowed to stir for 3 h and turned dark yellow. The yellow complex was filtered, washed with hot water, and dried in a vacuum

desiccator. [Decomp: ≥350°C; FT-IR (KBr, cm-1):$\nu = 3400$ and 3250(—CONH—); 3095(vinyl C—H stretch); 1680 (C═O carbonyl stretch); 1550 and 1420 (C═O carboxylate stretch, sym & anti-sym); 1250 (C—O stretch); 945 (UO_2^{2+} ion symmetric vibration); 890 (UO_2^{2+} ion anti-symetric vibration).]

Preparation of Uranyl-Imprinted Polymeric Microbeads

The uranyl-imprinted beads were prepared by dispersion polymerization technique. A typical suspension copolymerization procedure of P(MAGA-UO_2^{2+}-co-EGDMA) beads was given as follows. The dispersion medium was prepared by dissolving 0.2 -g polyvinylalcohol within 60 mL of distilled water, then 0.06 g of 2,2′-azobisisobutyronitrile (AIBN) was dissolved within monomer phase 7.0 mL/1.0 mmol in 4.0-mL ethanol/12.0-mL (EGDMA/MAGA-UO_2^{2+}/toluene). This solution was then transferred into the dispersion medium placed in a magnetically stirred (at a constant stirring rate of 600 rpm) glass polymerization reactor (100 mL), which was in a thermostatic water bath. The reactor was flushed by bubbling nitrogen and then was sealed. The reactor temperature was kept at 70°C for 6 h. Then, the polymerization was completed at 90°C in 3 h. After polymerization, the P(MAGA-UO_2^{2+}-co-EGDMA) beads were separated from the polymerization medium. The residuals (e.g., unconverted monomer, initiator) were removed by a cleaning procedure. The resulting microbeads were treated with 50/50 methanol/water, pH 3, for 24 h to remove the templates. The template-free polymers were treated with 100-mM EDTA (pH 7.0) in the shaker bath for 24 h and then 0.1-M $NaHCO_3$ to remove the uranyl ion. Briefly, beads were cleaned by washing solutions (i.e., a dilute HCl solution and a water–ethanol mixture) and dried in a vacuum oven at 70°C for 48 h. In the same way, nonimprinted microbeads were also prepared by using MAGA and EGDMA.

Characterization of P(MAGA-UO_2^{2+}-co-EGDMA) Microbeads

Swelling Tests

Water uptake properties of P(MAGA-UO_2^{2+}-co-EGDMA) beads were determined by volumetric method. In this method, the dry beads of 100 mg were placed in cylindrical tubes and the top point of the tube was marked. Then, the tube was filled with distilled water and the beads are allowed to swell at room temperature. The height of the beads were marked every

30 minutes. The height of swollen beads in the tube was used to calculate the swelling ratio by using the following formula:

$$\text{Swelling ratio}\,(\%) = [(h_{swollen} - h_{dry}) / h_{dry}] \times 100$$

Where $h_{swollen}$ is the height of the swollen beads and h_{dry} is the height of the dry beads in the tube.

Elemental Analysis

The amounts of C, H, and N of P(MAGA-co-EGDMA) and P(MAGA-UO_2^{2+}-co-EGDMA) microbeads were determined by elemental analysis by using Leco elemental analyzer (Model CHNS-932).

FTIR Studies

Fourier transform infrared spectroscopy (FTIR) spectra of P(MAGA-co-EGDMA) and P(MAGA-UO_2^{2+}-co-EGDMA) microbeads were obtained through the use of a FTIR spectrophotometer (Jasco Corparation, Japan; FT/IR-300 E).

Uranium Adsorption/Desorption

Adsorption of UO_2^{2+} ions from aqueous solutions was investigated in a batch experiments. Effects of the initial UO_2^{2+} ion concentration, pH of the medium on the adsorption rate, and adsorption capacity were studied. The suspensions were brought to the desired pH by adding sodium hydroxide and nitric acid. The pH was maintaned in a range of ± 0.1 units until equilibrium was attained. In all experiments, polymer concentration was kept constant at 50 mg/25 mL. The concentration of the metal ions in the aqueous phases after desired treatment periods were measured by using a graphite furnace atomic absorption and UV spectrophotometers. Deuterium background correction was used. The instrument response was periodically checked with known UO_2^{2+} ion solution standards. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin error. Adsorption

values (mg/g) were calculated as the difference in UO_2^{2+} ion concentration of the pre- and postadsorption solutions divided by the weight of dry microbeads.

Adsorbed UO_2^{2+} ions were desorbed by treatment with 0.1-M EDTA, 0.1-M $NaHCO_3$, and other solutions. The UO_2^{2+} adsorbed imprinted microbeads were placed in the desorption medium and stirred continuously at 600 rpm at room temperature for 2 h. The final UO_2^{2+} ion concentration in the aqueous phase was determined by spectrophotometrically. The desorption ratio was calculated from the amount of UO_2^{2+} ions adsorbed on the imprinted microbeads and the final UO_2^{2+} ion concentration in the desorption medium. To test the reusability of UO_2^{2+}-imprinted beads, UO_2^{2+} adsorption-desorption procedure was repeated ten times by using the same imprinted microbeads.

Selectivity Experiments

The batchwise selective adsorption experiments of Th(IV), Fe(III), and Mn(II) with respect to UO_2^{2+} were conducted using imprinted and nonimprinted polymers. The polymers (0.05 g) were added to 25 mL of aqueous solution of containing 100 mL Th(IV)/UO_2^{2+}, Fe(III)/UO_2^{2+}, and Mn(II)/UO_2^{2+} and placed in a sealed test tube. A solution (25 mL) containing 100 mg/L from each metal ion was treated with the UO_2^{2+} imprinted microbeads at a pH of 4.0 at room temperature, in the flasks stirred magnetically at 600 rpm. After adsorption equilibrium, the concentration of Fe(III) and Mn(II) ions in the remaining solution was measured by FAAS. Thorium was determined by spectrophotometric method. In the spectrophotometric determination of thorium, the complex equilibria of Th^{4+} with Lawsone (2-hydoxy-1,4-naphthoquinone, LAS)[28] were studied spectrophotometrically in 40% (v/v) ethyl alcohol water at 25°C and ionic strength of 0.1 M ($NaClO_4$). After the reaction of LAS with thorium, the absorbance of this complex solution was monitored at 440 nm against a reagent blank.

Distribution and selectivity coefficients of Th(IV), Fe(III), and Mn(II) with respect to UO_2^{2+} were calculated as explained as follows.

$$K_d = [(C_i - C_f)/C_f] \text{ X (volume of the solution, mL)/}$$

$$\text{(massofmicrobeads, g)}$$

where K_d, C_i, and C_f represent the distribution coefficient and initial and final solution concentrations, respectively. The selectivity coefficient for the binding of a metal ion in the presence of competitor species [(Eq. (1)] can be

obtained from equilibrium binding data[29,30] according to Eq. (2)

$$M_1(\text{solution}) + M_2(\text{sorbent}) <=> M_2(\text{solution}) + M_1(\text{sorbent}) \quad (1)$$

$$k = ([M_2]_{\text{solution}}[M_2]_{\text{sorbent}})/([M_1]_{\text{solution}}[M2]_{\text{sorbent}})$$

$$= Kd(UO_2^{2+})/K_d(X^{n+}) \quad (2)$$

where k is the selectivity coefficient and X^{n+} represents Th(IV), Fe(III), or Mn(II) ions. A comparison of the k values of the imprinted microbeads with those metal ions allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient k' [(Eq. (3)] can be defined as

$$k' = k_{\text{imprinted}}/k_{\text{control}} \quad (3)$$

RESULTS AND DISCUSSION

Properties of Uranyl-Imprinted Microbeads

P(MAGA-UO_2^{2+}-co-EGDMA) microbeads were spherical in shape with a size range of 80 to 120 μm in diameter. The specific surface area, which was determined with a BET apparatus, of P(MAGA-UO_2^{2+}-co-EGDMA) microbeads as found to be 14.6 m^2/g. The P(MAGA-UO_2^{2+}-co-EGDMA) microbeads are crosslinked hydrophilic matrices. The equilibrium swelling ratio of the P(MAGA-UO_2^{2+}-co-EGDMA) microbeads used in this study is 26.7%. It should be noted that these microbeads are a crosslinked structure, so the swelling ratio of this polymer is not so high. The amount of uranyl ion obtained after the treatment of polymeric microbeads by methanol/water, EDTA,s and $NaHCO_3$, was determined spectrophometrically and it was found that 0.86-mmol uranium was removed from the imprinted polymeric microbeads. This result was also supported by the elemental analysis results (Table 1). As seen in the table, when uranyl ion is removed from the polymer, the amounts of C, H, and N are high, as expected.

As mentioned before, MAGA was synthesized as the ligand. In the first step, MAGA was synthesized from glutamic acid and methacryloyl chloride. Then, uranyl ion was treated with MAGA to get MAGA-UO_2^{2+} complex monomer and poylmerized with EGDMA. The characteristic vibration bands of MAGA-UO_2^{2+} and P(MAGA-UO_2^{2+}-co-EGDMA) show similarity. FTIR spectra P(MAGA-UO_2^{2+}-co-EGDMA) microbeads are: FT-IR (KBr, cm-1):ν = 3460 and 3400(—CONH—); 1732 (C═O carbonyl stretch); 1643

Table 1. Elemental analysis results of microbeads before and after template removal.

	C (%)	H (%)	N (%)
UO_2^{2+}(Before template removal)	58.43	6.84	0.23
UO_2^{2+}(After template removal)	59.97	7.26	0.39

(amide I band); 1446 (amide II); 960 (UO_2^{2+} ion symmetric vibration); 895 (UO_2^{2+} ion anti-symetric vibration).

Adsorptive Separation of Uranium

Adsorption Rate

Figure 1 shows the adsorption capacity of uranyl ions by P(MAGA-UO_2^{2+}-co-EGDMA) microbeads as a function of time. High adsorption rates are observed at the beginning of adsorption and saturation values are reached within 75 minutes Adsorption of uranyl ions was rather fast, especially when the uranyl concentration was high.

A wide range of equilibrium adsorption times are reported with various sorbent systems in membrane and microsphere forms. For example,

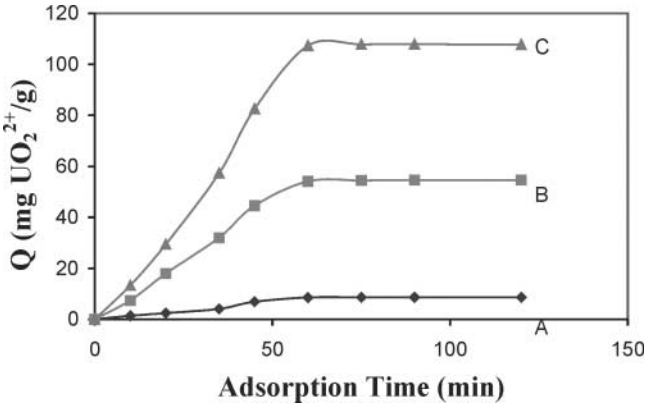

Figure 1. Adsorption rates of uranyl ions on the uranyl-imprinted beads, pH: 4.5. A. for 100 mg/L UO_2^{2+}. B. for 500 mg/L UO_2^{2+}. C. for 1000 mg/L UO_2^{2+}.

Denizli et al[31] got a 120-minute equilibrium time for Ni(II) using polyethyleneimine-attached poly(pchloromethylstyrene) beads. Reed and Matsumoto[32] used activated carbon as a cadmium sorbent and found 6 h as a equilibrium time. Poly(1-vinylimidazole) resin by radiation-induced polymerization with template Ni(II) ion was studies by Tsuchida et al.[33] Zn(II) imprinted 1,12-dodecanediol-O,O′-diphenyl phosphonic acid (DDDPA),[20] Cu(II) imprinted mesoporous sorbents was studies by Dai et al.[31] crosslinked polymeric sorbents of diethyl ester of vinylphosphonic acid with acrylic acid was studies by Kabanov.[34] These researchers report adsorption equilibrium that was attained within 1 h, 24 h, 12 h, and 1 h, respectively. Egawa studied uranium adsorption on polyacrylonitrile fibers containing amidoxime groups and reported a 7-h equilibrium adsorption time.[35]

Effects of Initial Concentration of Uranyl-Ion

Sorbents used in heavy metal removal are generally in particulate form. A wide variety of polymers having a range of adsorption capacities for uranyl ions are reported. Yamini et al reported that 4.033 mg of uranium was removed with octadecyl-bonded silica membrane disks modified with tri-n-octylphosphine oxide.[26] The maximum adsorption capacity of polyurethane foam grafted with glutamic acid (MSE-PMF) and amidoxime containing acrynitrile-divinylbenzene copolymer beads was found to be 10 mg/g of UO_2^{2+} 191.7 mg/g UO_2^{2+} by Hu and Reeves[36] and Nakayama et al,[37] respectively. Uranyl adsorption capacities of the hydrogels were determined by Özyürek et al[10] as 6 mg UO_2^{2+}/dry gel. Agrawal et al[38,39] introduced polymer supported calix[6] arene hydroxamic acid and calix[4] arene-semicarbazone resins for uranyl removal and obtained 96.59 mg/g and 2.98 mg/g resin, respectively. Figure 2 shows the adsorption capacities of the P(MAGA-UO_2^{2+}-co-EGDMA) microbeads for uranyl ion from aqueous solution. The amount of adsorption was increased when the initial uranyl ion concentration was increased until saturation was reached. The maximum adsorption capacity of the P(MAGA-UO_2^{2+}-co-EGDMA) microbeads was 181.0 mg/g.

Effects of pH

Metal ion adsorption onto specific adsorbents is pH-dependent. In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. The effect of pH on the uranyl ion adsorption of P(MAGA-UO_2^{2+}-co-EGDMA)

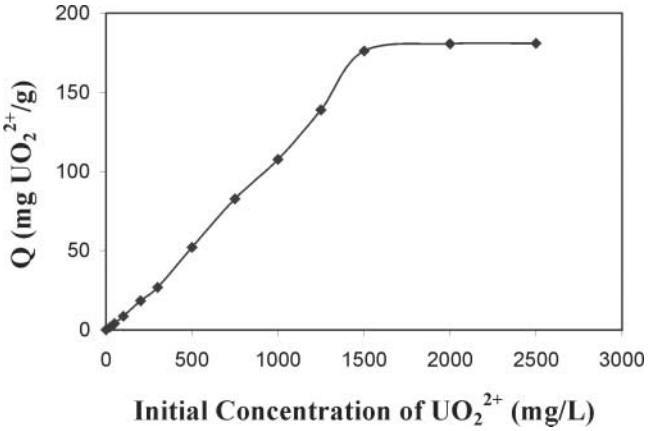

Figure 2. UO_2^{2+} ion adsorption capacity of the uranyl-imprinted microbeads, pH: 4.5. *The data present averages of the three repeated experiments.

microbeads is shown in Fig. 3. The UO_2^{2+}-imprinted microbeads exhibited a low affinity in acidic concentrations (pH $<$3.5) and a high affinity at pH 3.5. Imprinted microbeads adsorb the corresponding imprinted uranyl ion more effectively than do nonimprinted microbeads. The adsorption percentages increase with increasing pH on every microbead. This means that the carboxyl

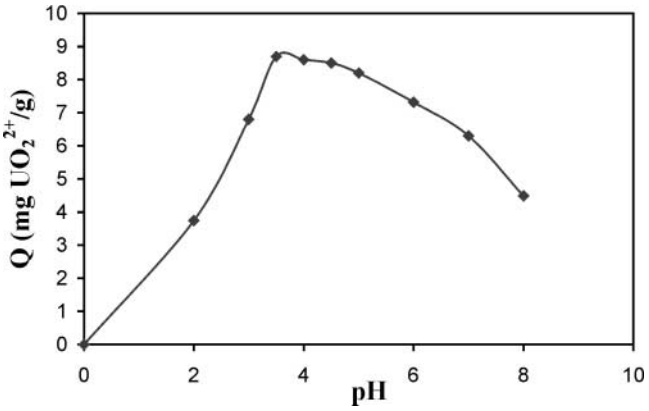

Figure 3. Effet of pH on the adsorption of uranyl ions and the uranyl-imprinted microbeads. Initial concentration of uranyl ions: 100 mg/L for UO_2^{2+}. *The data present averages of the three repeated experiments.

groups on the microbeads participitate in the uranyl ion binding in their oxidized carboxylate form. This is the reason for increasing of adsorption rate at lower pH. On the other hand, at higher values of pH, the uranyl ion may hydrolyze to form species such as UO_2OH^+, $UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)^{5+}$.[23] It may be though that these relatively big molecules cannot enter the holes, which have the same size and shape as UO_2^{2+}, so the adsorption ratio decreases.

Selectivity Studies vs. Th(IV), Fe(III), and Mn(II) Ions

Competitive adsorption of Th(IV)/UO_2^{2+}, Fe(III)/UO_2^{2+}, and Mn(II)/UO_2^{2+} from their couple mixture was also investigated in a batch system. Th(IV)/UO_2^{2+} was chosen as a competitive element because uranium and thorium often coexist in the minerals, products, and in even in waste water. Due to their similar behavior, determination and separation of uranium is a problem in the presence of thorium. Fe(III)/UO_2^{2+} and Mn(II)/UO_2^{2+} couples were chosen because these elements are in the same hard acid group and interfere each other. Table 2 summarizes K_d, k, and k′ values of Th(IV), Fe(III), and Mn(II) with respect to UO_2^{2+}. A comparison of the K_d values for the UO_2^{2+}-imprinted samples with the control samples for

Table 2. K_d, k, and k′ values of Th(IV), Fe(III), and Mn(II) with respect to UO_2^{2+}.

Beads	UO_2^{2+} (mg/L)	Th^{4+} (mg/L)	K_d (UO_2^{2+})	K_d (Th^{4+})	k	k′
Nonimprinted	100	100	19.8	4.54	4.36	—
UO_2^{2+} imprinted	100	100	172	3.52	48.9	11.2
Beads	UO_2^{2+} (mg/L)	Fe^{3+} (mg/L)	K_d (UO_2^{2+})	K_d (Fe^{3+})	k	K′
Nonimprinted	100	100	12.3	118.0	0.104	—
UO_2^{2+} imprinted	100	100	161.3	19.8	8.17	78.6
Beads	UO_2^{2+} (mg/L)	Mn^{2+} (mg/L)	K_d (UO_2^{2+})	K_d (Mn^{2+})	k	k′
Nonimprinted	100	100	17.6	102.0	0.172	—
UO_2^{2+} imprinted	100	100	169.3	10.7	15.8	91.9

Table 3. Uranium recovery by using different desorption agents.

Desorption reagent	Uranium recovery (%)
0.1-M HCl	86.9
0.1-M HNO_3	80.1
0.1-M Na_2CO_3	95.7
0.1-M $NaHCO_3$	96.1
0.1-M EDTA	92.6

the P(MAGA-UO_2^{2+}-co-EGDMA) microbeads shows an increase in K_d for UO_2^{2+} while K_d decreases for Th(IV), Fe(III), and Mn(II). The value of k' is greater than 1 for imprinted microbeads. A k' of 78.6 and 91.9 is, to the best of our knowledge, the highest value for the molecular imprinting of metal ions. We got 11.2 as a k' for the UO_2^{2+}/Th^{4+} couple, they even have a similar size. This means that UO_2^{2+} can be determined even in the presence of Th(IV).

Desorption Studies

Table 3 summarizes uransium recovery by using different desorption agents. Desorption ratios are very high (up to 96.1%). As seen in the table, when $NaHCO_3$, Na_2CO_3, and EDTA is used as a desorption agent, the percentage recovery is high and the coordination spheres of chelated UO_2^{2+} ions is disrupted and, subsequently, UO_2^{2+} ions are released from the uranyl templates into the desorption medium. This is because EDTA desorbs uranyl by chelating it, while $NaHCO_3$ and Na_2CO_3 do so by increasing the pH, which leads to the formation of the noncoordinating or weakly coordinating UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)^{5+}$.

CONCLUSION

We have shown that molecular imprinted polymer that contains poly[ethylene glycol dimethacrylatemetacryloylamidohistidine/UO_2^{2+}] [P(MAG-UO_2^{2+}-co-EGDMA)] is very selective and has high adsorption capacity for uranyl ion. A High adsorption rate was observed at the beginning of of the adsorption process and saturation values are reached within 75 minutes. The maximum UO_2^{2+} ion adsorption capacity of the P(MAG-UO_2^{2+}-co-EGDMA) microbeads was 181 mg/g. The adsorption

amount of UO_2^{2+} ion was maximum at pH 3.5. Competitive [Th(IV)/UO_2^{2+}, Fe(III)/UO_2^{2+}, and Mn(II)/UO_2^{2+}] adsorption studies showed that, P(MAGUO_2^{2+}-co-EGDMA) microbeads are only selective to uranyl ion, even in the presence of thorium and other metal ions. Distribution (K_d), selectivity (k), and relative selectivity (k′) coefficients were also calculated. The value of k′ was found, 11.2, 78.6, and 91.9 for Th(IV), Fe(III), and Mn(II), respectively. These k′ values are high values if they are compared with reported research values. It may be concluded from the results presented that P(MAG-UO_2^{2+}-co-EGDMA) microbeads can be effectively used for the specific removal of UO_2^{2+} ion from aqueous solutions by solid-phase extraction.

ACKNOWLEDGMENTS

This work was partly supported by TUBITAK (Project No: IÇTAG-Ç010).

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Received August 2002
Revised January 2003