Journal of Hazardous Materials 175 (2010) 193–197

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Synthesis and characterization of new ion-imprinted polymer for separation and preconcentration of uranyl (UO_2^{2+}) ions

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ARTICLE INFO

Article history:
Received 16 April 2009
Received in revised form
29 September 2009
Accepted 29 September 2009
Available online 6 October 2009

Keywords:
Ion-imprinted polymer
Uranyl ion
Separation
Preconcentration
N,N′-Ethylenebis(pyridoxylideneiminato)

ABSTRACT

UO_2^{2+} ion-imprinted polymer materials used for solid-phase extraction were prepared by copolymerization of a ternary complex of uranyl ions with styrene and divinyl benzene in the presence of 2,2′-azobisisobutyronitrile. The imprinted particles were leached by HCl 6 M. Various parameters in polymerization steps such as DVB/STY ratio, time of polymerization and temperature of polymerization were varied to achieve the most efficient uranyl-imprinted polymer. X-ray diffraction (XRD), infra-red spectroscopy (IR), thermo gravimetric analysis (TGA), UV–vis and nitrogen sorption were used to characterize the polymer particles. The XRD results showed that uranyl ions were completely removed from the polymer after leaching process. IR Analysis indicated that the N,N′-ethylenebis(pyridoxylideneiminato) remained intact in the polymer even after leaching. Some parameters such as pH, weight of the polymer, elution time, eluent volume and aqueous phase volume which affects the efficiency of the polymer were studied.

1. Introduction

The technique of molecular imprinting has attracted much attention as a method for high-selective host polymer [1]. The technique basically consists of three steps: (i) synthesis of functional vinyl monomer that can interact with a target template, (ii) free radical polymerization of the vinyl monomers with cross-linking reagent in the presence of the template and (iii) removal of the template from the cross-linked copolymer resin. This method has been demonstrated to be effective for metal ions, saccharides, amino acid derivatives and other organic compounds of low molecular weight [2]. Ion-imprinted polymers (IIPs) are similar to molecular imprinted polymers (MIPs), but they recognize metal ions after imprinting, while retaining all the virtues of MIPs [3,4].

So far, various separation/preconcentration techniques have been used for uranyl ion such as liquid-liquid extraction [5–7] and solid-phase extraction, using cation exchangers, chemically modified [8] or impregnated silica, active carbon [9] and Amberlite XAD resins. During the last decade, some interest has been shown for preparation of uranyl-imprinted polymers. Sadeghi and Akbarzadeh have reported a new imprinted sorbent for preparation and preconcentration of UO_2^{2+} [10]. Trapping method, which involves the use of a vinylated and non-vinylated chelating agents inside the polymer matrix were reported by Gladis and Rao [11–14]. In this study, an ion-imprinted polymer sorbent is prepared for preconcentration and separation of uranyl (UO_2^{2+}) ions.

2. Experimental

2.1. Instruments and apparatus

A Varian Liberty 150 AX Turbo model inductively coupled plasma-atomic emission spectroscopy (ICP-EAS) and Varian SPECTRA AA-200 atomic absorption spectroscopy (AAS) were used for the determination of metal ions. The IR spectra (4000–400 cm^{-1}) in KBr were recorded with the aid of a Bruker spectrometer. Thermogravimetric analysis was carried out using the Rheometric scientific simultaneous thermal analyzer. The XRD patterns were obtained with Cu-kα X-ray source and a Philips PW 1710 diffractometer (Netherlands). A Varian Cary131 model computer-controlled double beam UV–vis spectrophotometer was utilized to prepare the UV–vis spectrum of the reaction mixtures. Nitrogen sorption studies were made with a Quantachrome NOVA instrument.

2.2. Reagents and materials

Uranyl nitrate (6-hydrate), pyridoxal hydrochloride, ethylendiamin, 4-vinyl pyridine, styrene, divinylbenzene, 2-methoxy ethanol, dimethyl sulfoxide (DMSO) and 2,2′-

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doi:10.1016/j.jhazmat.2009.09.148

azobisisobutyronitrile were obtained from Merck Co. All the reagents and chemicals used were of analytical grade.

2.3. Synthesis of uranyl-imprinted polymer

Synthesis of uranyl-imprinted polymer was performed in three steps: (i) synthesis of $[UO_2(pyr_2en)DMSO]Cl_2$ {pyr_2en=N,N′-ethylenebis(pyridoxylideneiminato)} binary complex, (ii) ternary complex formation of $[UO_2(pyr_2en)DMSO]Cl_2$ with 4-vinylpyridine, and (iii) copolymerization of ternary complex with styrene as functional monomer and divinylbenzen as cross-linking agent.

2.3.1. Synthesis of $[UO_2(pyr_2en)DMSO]Cl_2$ binary complex

Synthesis of $[UO_2(pyr_2en)DMSO]Cl_2$ was performed in two steps according to [15]: (i) preparation of N,N′-ethylenebis(pyridoxylideneiminato) and (ii) preparation of $[UO_2(pyr_2en)DMSO]Cl_2$.

2.3.1.1. Preparation of N,N′-ethylenebis(pyridoxylideneiminato). After dissolving 0.203 g of pyridoxal hydrochloride in 50 ml of methanol, ethylenediamine (0.35 g) was added dropwise. The solution turned deep yellow immediately. The mixture was refluxed at 60 °C for 1 h. Small yellow crystals were isolated from solution at room temperature after 2 days with 90% yield.

2.3.1.2. Preparation of $[UO_2(pyr_2en)DMSO]Cl_2$. A methanolic solution containing 0.140 g of N,N′-ethylenebis(pyridoxylideneiminato) and 0.98 g of $UO_2(NO_3)_2{\cdot}6H_2O$ was stirred under reflux for 30 min. A red precipitate was separated after 3 days, dried and recrystallized from DMSO. Red prismatic crystals were obtained after 2 days with 85% yield.

2.3.2. Ternary complex formation of $[UO_2(pyr_2en)DMSO]Cl_2$ with 4-vinylpyridine(VP)

The binary complex from the last step was dissolved in 6 ml DMSO and then 0.390 mmol VP (0.041 g) was added to this solution and stirred for 1 h to give deep red ternary complex of $[UO_2(pyr_2en)DMSO]Cl_2$ with 4-vinylpyridine.

2.3.3. Copolymerization of ternary complex with styrene as functional monomer and divinylbenzene as cross-linking agent

The polymerization mixture involved blending of 7.8 mmol (0.812 g) STY, 7.8 mmol (1.015 g) DVB, 4 ml 2-methoxy ethanol, 6 ml solution of ternary complex in DMSO (from the last step) and 100 mg AIBN, which was stirred for 1 h to complete the reaction. The prepared solution was cooled to 0 °C, purged with N_2 for 10 min and heated at 60 °C during stirring for 18 h.

Afterwards, the obtained polymer particles were ground in a mortar and dried in oven at 60 °C for 2 h. About 4 g of these powdered particles were subjected to leaching with 100 ml of 50% aqueous solution HCl for 6 h to obtain uranyl IIP particles. The control polymer (CP) particles were prepared in a similar way as that of the IIP preparation, but without the imprinted ion, uranyl (UO_2^{2+}). The resultant CP particles were compared with IIP particles in terms of extraction ability.

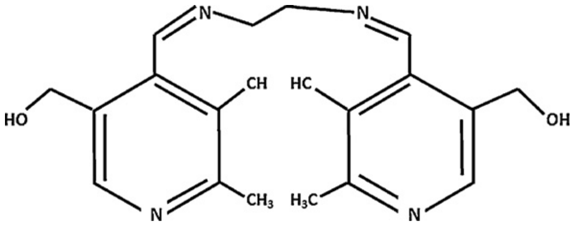

Fig. 1. N,N′-Ethylenebis(pyridoxylideneiminato).

2.4. General procedure for uranyl extraction

The extraction studies of the UO_2^{2+} ions with the prepared imprinted polymer were carried out by batch experiments as follows: Aliquots of uranyl solution (100 ml) in the concentration range 0.005–2 mg l^{-1} were treated with 100 mg of polymer particles at various pH. The pH of the suspensions was adjusted to desired values by adding sodium hydroxide or nitric acid. The suspension was stirred for preselected periods of time, using a magnetic stirrer. The uranyl ions were eluted from the IIP particles using 25 ml of 1.0 M HCl, through a filter paper. Their content in the eluent was determined with ICP-AES.

The distribution coefficients (k_d) of UO_2^{2+} ions were determined by the following equation:

$$k_d = \frac{(C_i - C_f)V}{C_f W}$$

where V is the volume of initial solution and W is the mass of IIP materials, C_i and C_f are initial and final concentrations of solutions. The percentage of extraction %E was calculated using the following equation:

$$\%E = \frac{C_i - C_f}{C_i} \times 100$$

3. Results and discussion

3.1. Preparation of the uranyl-imprinted polymer

The complexation of uranyl with N,N-ethylenebis(pyridoxylideneiminato) as ligand (Fig. 1) was reported earlier [15]. In order to obtain specific imprinted sites in polymer particles, several polymers with different compositions were synthesized (Table 1).

For comparison, in a preliminary experiment, the preconcentration of 100 ml solution of 0.05 mg l^{-1} uranyl at pH 7 ± .4 was carried out using the prepared polymer particles. The results are given in Fig. 2.

Although under preliminary experimental conditions the preconcentration was not quantitative in all cases but in the case of IIP1 corresponding to 1:1 molar ratio of STY:DVB, a higher percentage of enrichment of uranyl ions was achieved. It was found that if the DVB to STY molar ratio is greater than one, the desire polymer structure, which allows the complete trapping of the UO_2^{2+} ion is

Table 1
Recipes for the preparation of the control and ion-imprinted polymer.

	UO_2^{2+} (mmol)	VP (mmol)	STY (mmol)	DVB (mmol)	AIBN (mg)
IIP1	1	2	40	40	100
CP1	–	2	40	40	100
IIP2	1	2	26.6	53.3	100
CP2	–	2	26.6	53.3	100
IIP3	1	2	53.3	26.6	100
CP3	–	2	53.3	26.6	100

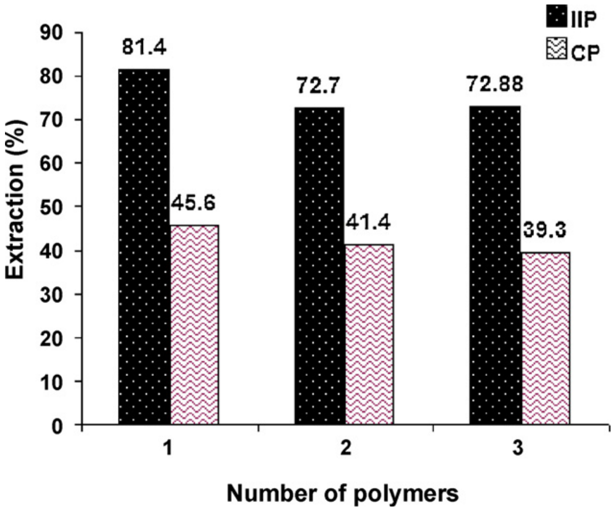

Fig. 2. Extraction percent of uranyl ions using synthesized uranyl-imprinted polymer according to Table 1 (containing 0.1 g of particles; 100 ml of 0.05 mg l^{-1} uranyl solution; 1 h preconcentration time).

not achieved as a result of the high concentration of cross-linking agent value and also fast polymerization.

3.2. Characterization studies

3.2.1. IR spectra

The IR spectra of the leached and unleached IIP particles were recorded in the range of 4000–400 cm^{-1} and are shown in Fig. 3.

All polymers show similar IR spectra, indicating the similarity in the backbone structure of leached and unleached polymers. The peaks near 700 and 1600 cm^{-1} are attributed to ν_{C-H} and $\nu_{C=C}$ in aromatic rings, and the peak near 1450 cm^{-1} is due to ν_{CH_3} both in leached and unleached polymers, illustrating that N,N′-ethylenebis(pyridoxylideneiminato) was kept intact in the polymer even after leaching.

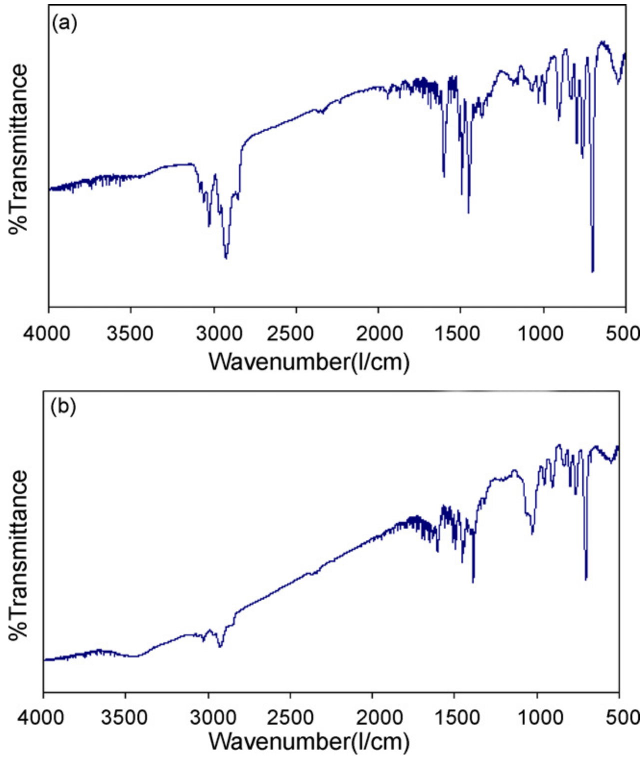

Fig. 3. IR spectra of the leached (a) and unleached (b) IIP particles.

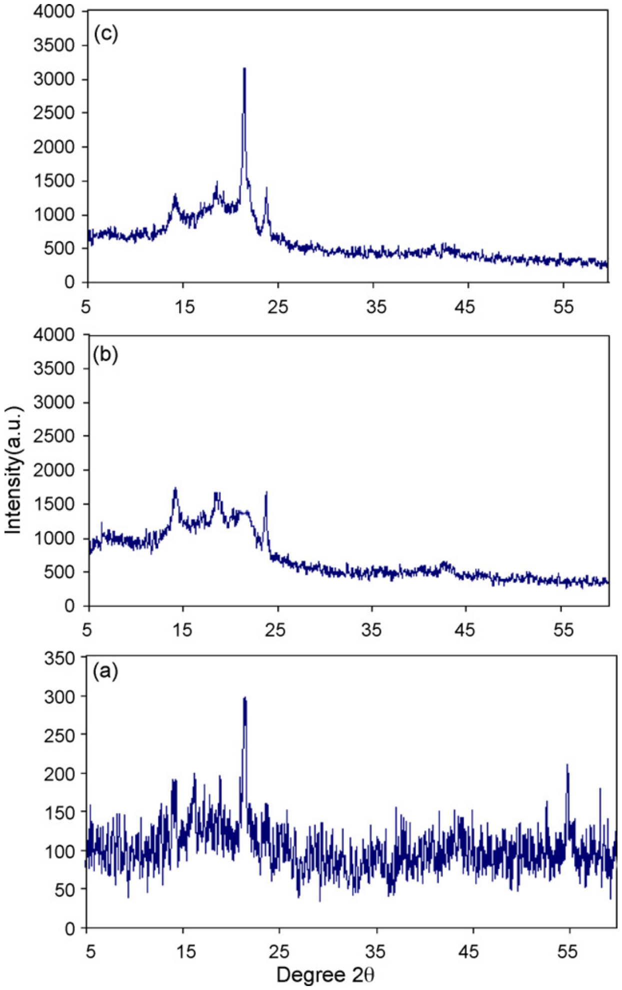

Fig. 4. X-ray diffraction patterns for uranyl nitrate (a), leached (b) and unleached (c) polymer particles.

3.2.2. X-ray diffraction (XRD)

The XRD patterns of the uranyl nitrate (a), leached (b) and unleached (c) IIP particles are given in Fig. 4. XRD of the leached and unleached IIP particles show similar patterns and the peak related to uranyl nitrate, as can be seen in patterns (a) and (c), are absent in pattern (b), indicating that the uranyl ions were completely removed during the leaching.

3.2.3. Thermal analysis (TGA)

Thermal stability of the leached and unleached polymer particles was studied by performing thermo gravimetric analysis (Fig. 5).

TGA plots with identical characteristics were obtained for the leached and unleached polymer particles. It seems that in the temperature range of 250–450 °C decomposition of $[UO_2(pyr_2en)DMSO]Cl_2$ occurs as its melting point is about 270 °C. All the materials were completely decomposed at about 627 °C.

3.2.4. UV–vis spectral

The formation of binary complex $[UO_2(pyr_2en)DMSO]Cl_2$ was confirmed as reported [15]. The UV–vis absorption spectral in methanol is shown in Fig. 6. It shows the change of λ_{max} in curve (b) for N,N′-ethylenebis(pyridoxylideneiminato) to curve (c) for binary complex of $[UO_2(pyr_2en)DMSO]Cl_2$ and curve (d) for ternary complex of $[UO_2(pyr_2en)DMSO]Cl_2$ with 4-vinylpyridine, and confirms

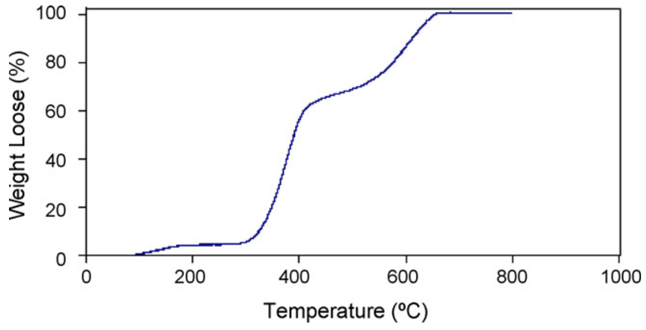

Fig. 5. Thermogram of IIP polymer particles.

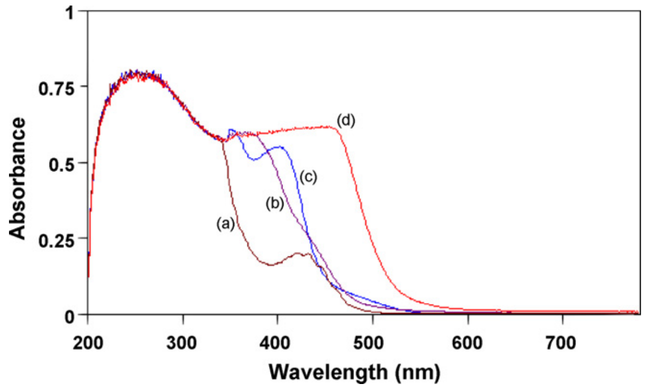

Fig. 6. UV–vis absorption spectra of UO_2^{2+} (a), N,N′-ethylenebis(pyridoxylideneiminato) (b), [UO_2(pyr$_2$en)DMSO]Cl_2 (c), [UO_2(pyr$_2$en)DMSO]Cl_2 with VP (d) in methanol.

the formation of ternary complex.

3.2.5. *Nitrogen sorption*

The synthesized IIP particles were characterized using nitrogen sorption studies, in order to know the surface properties of the leached and unleached polymer particles. The surface area was determined by applying the BET equation. Data are recorded in Table 2 for the leached and unleached polymer particles. It is clearly seen that porosity changes after the removal of uranyl ions from the IIP particles.

3.3. *Optimization of sorption and elution of uranyl ion using IIP1 particles employing batch method*

In order to optimize conditions for obtaining high efficiency in preconcentration of uranyl ions by the proposed IIP1, it is necessary to adjust several factors including eluent volume, pH, sample volume, polymer weight, preconcentration, and elution time. The percentage recovery of uranyl ions was calculated from the ICP-AES results. A series of solutions with the volume of 100 ml and uranyl concentration of 0.05 mg l^{-1} were prepared. The pH values of these solutions were adjusted between 5.0 and 9.0. The recommended procedure was applied [4]. It is found that the uranyl sorption is constant, taking its maximum value at pH about 7.0, as can be seen in Fig. 7. In the subsequent work, the pH was adjusted to 7.0 ± 0.4.

Table 2
Nitrogen sorption data for leached and unleached IIP particles.

	Leached IIP particles	Unleached IIP particles
BET surface area (m^2/g)	33.2	18.5
Pore volume (cc/g)	0.05	0.02
Pore diameter (Å)	23.0	23.0

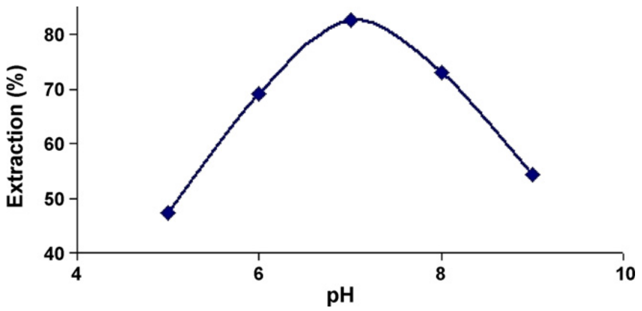

Fig. 7. pH effect on the preconcentration of the uranyl ion using leached IIP1 particles.

The effect of the weight of polymer particles on the enrichment percentage is shown in Fig. 8.

As recorded in Fig. 8, the changes in the extraction percentage in the range of 0.05–0.5 g are very small and it seems that about 0.1 ± .02 g of polymer particles can be effective for enrichment. All the other parameters influencing the preconcentration of UO_2^{2+} ions with the CP1 and IIP1 particles were systematically evaluated. The corresponding results are recorded in Table 3. It can be seen that the best condition for preconcentration occurs at about 0.1 ± 0.02 g of polymer particles used at pH 7. In this condition, the optimum elution time and eluent volume were 60 min and 30 ml, respectively. The best structure for polymer can be obtained at the polymerization time of about 18 h at 60 °C.

3.4. *Selectivity*

Selectivity coefficient of uranyl ions over other inorganic cations that coexisted with uranyl ions in the solution were studied by batch procedure. The IIP particles were tested for separation of uranyl ions from Th^{4+}, Nd^{3+}, Eu^{3+}, Cu^{2+}, Zn^{2+}, Mo^{2+} ions, either individually or in mixture. The concentration of transition metals was determined by atomic absorption spectroscopy (AAS) or ICP. The selectivity of the uranyl ions versus another cation was determined by the ratio of the two distribution coefficients, $k_{\mathrm{dUO_2}^{2+}}$ and $k_{\mathrm{dM}^{n+}}$, which is referred as selectivity factor:

$$\alpha = \frac{k_{\mathrm{dUO_2}^{2+}}}{k_{\mathrm{dM}^{n+}}}$$

The obtained results are summarized in Table 4.

It is clear from the results that the quantitative separation of uranyl ions from Th^{4+}, Nd^{3+}, Eu^{3+}, Cu^{2+}, Zn^{2+}, Mo^{2+} are possible. The reduction in the selectivity factor from Cu^{2+}, Zn^{2+}, Mo^{2+} to Eu^{3+},

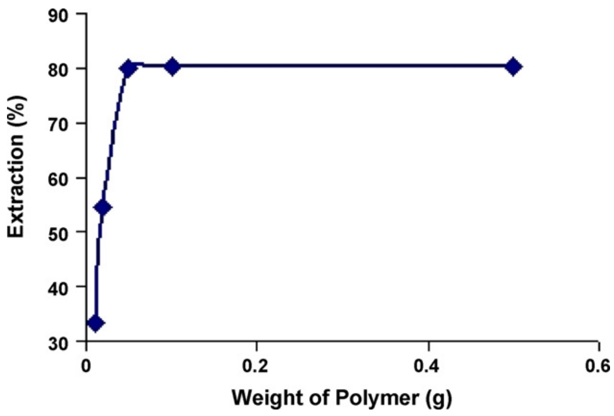

Fig. 8. Effect of polymer particles weight on the preconcentration of uranyl ions using leached IIP1 polymer particles.

Table 3
Effect of various parameters on the extraction percentage of uranyl ion using IIP1 and CP1 particles.

Parameter	Extraction (%)	
	CP1	IIP1
Weight of polymer (g)		
0.01	35.9	33.2
0.02	37.6	54.6
0.05	40.2	79.9
0.1	44.8	80.1
0.5	45.1	80.4
pH		
5	37.2	47.2
6	40.5	69.1
7	46.0	82.7
8	42.1	73.1
9	39.3	54.2
Preconcentration time (min)		
5	37.2	53.8
10	43.2	77.6
15	44.9	79.6
30	46.2	80.1
45	45.1	80.3
60	47	80.6
Elution time (min)		
10	40.2	44.9
20	56.2	59.7
30	60.9	72.3
60	71.5	98.2
Eluent volume (ml)		
5	40.2	51.3
10	51.1	62.4
20	60.9	75.7
30	71.1	99.1
Sample volume (ml)		
20	39.4	75.3
50	44.7	81.4
100	45.1	82.1
200	45.2	81.7
500	38.5	74.3
1000	32.1	70.2
Temperature of polymerization (based on 24 h polymerization, °C)		
55	–	80.0
60	–	81.1
65	–	73.6
70	–	68.6
Time of polymerization (h)		
2	–	33.8
5	–	67.6
10	–	75.8
18	–	80.3
24	–	80.7

Table 4
Distribution coefficient and selectivity coefficients of leached IIP particles.

Ion	Distribution coefficient (k_d, ml g^{-1})	Selectivity factor (α)
UO_2^{2+}	886.3	–
Th^{4+}	44.1	20.0
Nd^{3+}	30.1	29.3
Eu^{3+}	17.2	51.5
Cu^{2+}	3.2	276.9
Zn^{2+}	4.0	218.8
Mo^{2+}	2.0	426.1

Nd^{3+}, Th^{4+} is due to the ability of reaction for Th^{4+}, Nd^{3+}, Eu^{3+} with N,N′-ethylenebis(pyridoxylideneiminato) [16], but the present IIP synthesized for the UO_2^{2+} has a higher selectivity for this ion due to the match charge, coordination number, coordination geometry, and the pores size inside the imprinted polymer.

4. Conclusion

In the present work, a ternary complex of UO_2^{2+} with N,N′-ethylenebis(pyridoxylideneiminato) and 4-vinylpyridine was synthesized, and polymerized with DVB and STY. Various parameters of the structure of polymer particles and best conditions for preconcentration were studied. The selectivity factor of polymer particles relative to Th^{4+}, Nd^{3+}, Eu^{3+}, Cu^{2+}, Zn^{2+}, Mo^{2+} was determined. Due to high selectivity shown by this new material for uranyl ions, it has been successfully employed for the selective separation and preconcentration of uranyl ions from aqueous systems.

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