# Ion Imprinted Affinity Cryogels for the Selective Adsorption Uranium in Real Samples

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**ABSTRACT:** *In this article, selective adsorption of U(VI) in aqueous solutions in the presence various lanthanide ions by using U(VI)-imprinted cryogel polymer was conducted. For this purpose, the prepared pHEMA-$(MAH)_3$-U(VI) cryogel polymer by free radical polymerization method. U(VI) was desorbed with 5.0 mol/L $HNO_3$ and thus U(VI)-imrinted were created onto p-HEMA-$(MAH)_3$ cryogel polymer. To determine the optimum conditions, in the process of selective adsorption of U(VI) ion to U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer, some parameters such as pH, flow rate, initial U(VI) concentration were investigated. Under the optimum conditions, the maximum adsorption capacity was obtained as 74.80 mg/g. Selectivity studies were also carried out in the presence of Nd(III), La(III) and Y(III) ions using U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer. The obtained adsorption order under competitive conditions was U(VI) > La(III) > Y(III) > Nd(III).*

**KEYWORDS:** *U(VI)-imprinted cryogel polymer; p-HEMA-$(MAH)_3$; Selective adsorption; Purification.*

## INTRODUCTION

Uranium is an important material in nuclear science and an important actinide in radioactive waste water and environmental samples [1]. Uranium is a natural element that quite effective in the nuclear industry and particularly as a fuel for electricity generation by nuclear power plants [2]. Studies on uranium-containing rare earth minerals are causing uranium-containing radioactive pollutants [3,4,5,6]. Therefore, the solvent extraction and separation of Uranium from rare earth minerals is quite important for the environmental protection [7].

Uranium is the most important fuel element used in nuclear reactors. Therefore, the recovery of Uranium is of great importance for the sustainable development of nuclear industry [8]. The content of uranium in the earth's crust is limited [9]. Anticipating the shortage of nuclear fuels in near future, the selective recovery of Uranium becomes necessary for the sustainable development of nuclear energy [10].

The removal of uranium from the body has been studied by a number of investigators. 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

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for the determination of uranium. Although liquid–liquid extraction has been widely used [11], it is time consuming. Extraction chromatography [12], solid-phase extraction [13,14], supercritical fluid extraction [15], ion exchange [16] and adsorbents [17,18] 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 [19, 20, 21], 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 rare earth elements [22- 24].

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 [25-27].

Molecular imprinting is a new technique has attracted the attention of researchers for effective recognation of chemical and biological molecules including aminoacids, proteins, enzymes, DNA, drugs and metal ions [28-31]. This technique allows selective and sensitive recognition of chosen target molecule by leaving artificial imprinted cavities in polymer matrix that provides high affinity to target molecule. To synthesize molecularly imprinted polymer, the template molecule and functional monomers which can arrange around template are complexed interactively before polymerization. Then the rigid polymer matrix is obtained by polymerization of formed pre-complex and cross-linker reagent. After removal of template molecule from the polymer with suitable desorption agent, the cavities remaining in the polymer that are complementary in shape, size and chemical functionality to the template. Consequently, the resultant polymer able to recognizes and rebinds selectively the template or other molecules that are chemically related to the template [32]. This technique is used in many applications such as selectivity recognation and seperation [33-36], drug delivery systems [37], catalysis [38], sensor technology [39]. In addition, ion imprinted polymers (IIPs) have been used for the selective removal of metal ions from different matrices [40-48].

In this study, the selective adsorption of U(VI) in aqueous solutions and soil certified reference material in the presence of other lanthanide ions such as Nd(III), La(III) and Y(III) was performed by using U(VI)-imprinted pHEMA-$(MAH)_3$ cryogel polymer. For this purpose, U(VI) was complexed with N-methacryloyl-L-histidine methyl ester (MAH) and the prepared $(MAH)_3$-U(VI) complex monomer was polymerized with 2- hydroxyethyl methacrylate (HEMA) cryogel to prepare pHEMA-$(MAH)_3$-U(VI) cryogel polymer by free radical polymerization method. U(VI) was desorbed with 5.0 mol/L $HNO_3$ and thus were created U(VI) imprinted on to p-HEMA-$(MAH)_3$ cryogel polymer. In the process of selective adsorption of U(VI) ion to U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer, several factors such as medium pH, flow rate, initial U(VI) concentration were investigated to determine optimum conditions. Selectivity studies were also carried out in the presence of Nd(III), La(III) and Y(III) ions using U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer. The obtained adsorption order under competitive conditions was U(VI) > La(III) >Y(III) > Nd(III).

## EXPERIMENTAL SECTION

### *Chemicals and Reagents*

Methacryloyl cloride (purum, dist., ≥97.0% (GC), contains ~0.02% 2,6-di-tert-butyl-4-methylphenol as stabilizer), L-histidine (ReagentPlus®, ≥99%), 2-Hydroxyethyl methacrylate (HEMA) (≥99%, contains ≤50 ppm monomethyl ether hydroquinone as inhibitör), N,N,N,N-tetramethylethylenediamine (TEMED) (BioReagent, suitable for electrophoresis, ~99%), N,N-methylenebisacrylamide (MBAAm) (99%), Uranyl nitrate (extra pure, ≥99%), Lanthanium(III) nitrate hexahydrate (extra pure, ≥99%), Neodymium(III) nitrate hexahydrate (extra pure, ≥99%), Yttrium(III) nitrate hexahydrate (extra pure, ≥99%), Ammonium persulfate (APS) (reagent grade, 98%) and all organic solvents were provided from Sigma-Aldrich (Steinheim, Germany).

### *Instrumentation*

The analysis of the U(VI) and the other lanthanide ions was performed using a Agilent 7700 Series

inductively coupled plasma-mass spectroscopy (ICP-MS). System with the following parameters: RF Power= 1600 W, sampling depth= 5.3 mm, analyzer pressure= $7{,}92x10^{-5}$ Pa, helium flow in the collision cell= 4.98 mL/min and plasma temperature= 9883 K. the measurements were done with three replicates (95% confidence level). A Perkin Elmer model Spectrum 400 FT-IR spectrometer was used for the Fourier transform infrared (FT-IR) measurements. Scanning electron microscopy (SEM) analyses were carried out by using a FEI Quanta FEG 250 SEM system.

***Preparation of U(VI)-Imprinted and Non-İmprinted p-HEMA-(MAH)$_3$ Cryogel Polymer***

*Synthesis of N-methacryloyl-L-histidine methyl ester (MAH)*

The preparation and characterization of N-methacryloyl-(L)-histidine methyl ester (MAH) was reported elsewhere [49]. The following procedure was applied for the synthesis of MAH monomer: 5.2 g of L-histidine methylester and 0.22 g of hydroquinone were dissolved in 150 mL of $CH_2Cl_2$ solution. Solution was cooled down to 0 $^0$C. 12.83 g triethylamine was added to the solution. 4.0 mL of methacryloyl chloride was poured slowly into this solution under nitrogen atmosphere and then this solution was stirred magnetically at room temperature for 1 h. At the end of this chemical reaction period, unreacted methacryloyl chloride was extracted with 10% NaOH. Aqueous phase was evaporated in a rotary evaporator. MAH was crystallized in 20 mL (1:1) ethanol and ethyl acetate. The reaction efficiency was determined as 84% in the stoichiometric calculations based on the amount of reagents added to the reaction medium and the amount of MAH monomer obtained as a result of the process. In addition, it was determined that the purity of MAH monomer synthesized as a result of the characterization processes was greater than 98%.

***Preparation of (MAH)$_3$-U(VI) Complex Monomer***

For preparation $(MAH)_3$-U(VI) complex monomer, MAH (0.669 mg, 3.0 mmol) was dissolved in deionized water. After slow addition of $UO_2(NO_3)_2$ (0.394 mg, 1.0 mmol) to this solution, the solution was stirred for 24 h at room temperature. The obtained complex monomer was then filtered and extensive washed with EtOH and deionized $H_2O$. Then, it was dried at 50 $^o$C for 24 h. For the yield of the synthesis of the synthesized MAH-Th(VI) complex monomer, it was initially determined by ICP-MS analysis of the remaining Th(VI) in the medium which was added to the medium and the complex formation yield was determined to be greater than 95%.

***Synthesis of p-HEMA-(MAH)$_3$-U(VI) (IIP) and p-HEMA-(MAH)$_3$ (NIP) Cryogel Polymer***

p-HEMA-$(MAH)_3$-U(VI) and p-HEMA-$(MAH)_3$ cryogel polymers was prepared according to a previously reported method [50]. For this purpose, 0.25 g MBAAm was dissolved in deionized $H_2O$, and then 2.0 mL HEMA and 2.0 mL $(MAH)_3$-U(VI) complex monomer were mixed with this solution. Initiator APS (25 mg)/TEMED (25 µl) was added and the final mixture was placed into a syringe closed with parafilm and allowed to polymerize at -18 °C for 24 h. The frozen solution was allowed to thaw at room temperature. Finally, the prepared imprinted cryogel polymer was washed with 100 mL (1:1) EtOH and deionized $H_2O$ to remove impurities, which was then stored at +4 °C. Non-imprinted polymer were prepared in the same way but in the absence of the template.

***Removal of U(VI) from p-HEMA-(MAH)$_3$-U(VI) Cryogel Polymer***

To obtain the 3-D cavities for desorption of U(VI), the template U(VI) was successfully desorbed from the p-HEMA-$(MAH)_3$-U(VI) cryogel polymer (Fig. 1). For this purpose, the cryogel polymer was desorbed with 10 mL 5.0 mol.L$^{-1}$ $HNO_3$ as the desorbtion solvent for 1 h by using a peristaltic pump. This washing step was repeated until no U(VI) was determined in the desorption solvent.

## CHARACTERIZATION STUDIES

MAH monomer and prepared $(MAH)_3$-U(VI) complex monomer were characterized by FT-IR spectroscopy, whereas U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer were characterized by FT-IR spectroscopy and SEM technique.

To obtain FT-IR spectrum U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer, KBr was mixed with the dried polymer particles and pressed into a pellet form, and the spectra were then recorded.

For the SEM analysis of U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer were covered on the surface of platinum and coated with gold (thicknes of 20 nm). Then, SEM analyses were carried out.

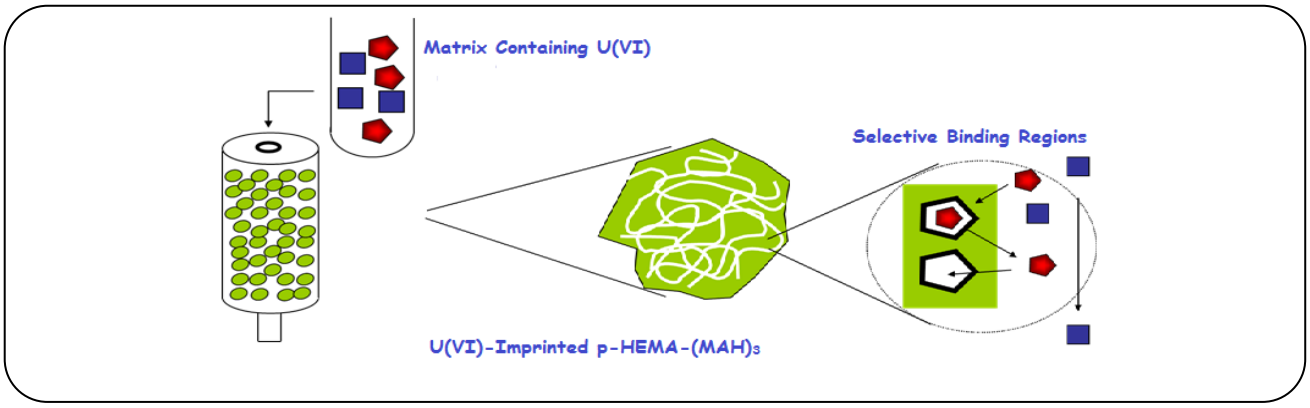


***Fig. 1: The prepared U(VI)-Imprinted column system and Selective Separation Scheme of U(VI).***

To calculate the swelling ratio of p-HEMA-$(MAH)_3$ cryogel polymer, the cryogel was dried and weighed until constant weight ($m_{dried}$). Then, it was placed in a 30 mL vial containing distilled water and kept at 25°C for 2 h. The cryogel was removed from water, wiped by a filter paper and weighed again ($m_{wet}$). The swelling ratio was calculated according to;

$$S = m_{wet} - m_{dried} / m_{dried} \quad (1)$$

For the measurement of macroporosity percentage (M%) of cryogels, the mass of water-saturated cryogels ($m_{wet}$) was weighed. The cryogel was squeezed to remove free water which is found in the pores ($m_{squeezed}$), and the mass of cryogel without water was weighted. M% was calculated according to;

$$m\% = m_{wet} - m_{queezed} / m_{wet} \quad (2)$$

***Adsorption Studies of U(VI) Ion to U(VI)-imprinted (IIP) and Non-imprinted (NIP) Cryogel Polymer***

Continuous column system was used to adsorption U(VI) to U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer (IIP) and non-imprinted p-HEMA-$(MAH)_3$ cryogel polymer (NIP). For this purpose, firstly, columns containing IIP and NIP was washed with deinozed $H_2O$ and equilibrated with 0.1 mol/L phosphate buffer at pH. 7.0. Then, aqueous solution of U(VI) was passed through the columns containing IIP and NIP at 1 mL/min flow rate for 1 h. The amounts of U(VI) was determined by ICP-MS. Then, 5.0 mol/L $HNO_3$ was used to desorption of U(VI) bound to the IIP and NIP. Sevaral factors such as pH, flow rate and initial U(VI) concentration were also investigated to obtain the optimum conditions for the adsorption of U(VI). 10 ppm U(VI) solutions in different pH values (pH 3 to 10) was passed through the columns containing IIP and NIP at 1 mL/min flow rate for 1 h in order to test pH influence on U(VI) adsorption to the IIP and NIP. Then, the samples came out from the column were analyzed by ICP-MS. The flow rates between 1.0 mL/min and 5.0 mL/min were applied for the investigation of the effects of these parameters on the adsorption of U(VI). The initial U(VI) concentration was varied between 10 ppm and 2000 ppm to determine maximum adsorption capacity.

***Selectivity Study***

The selectivity of the prepared U(VI)-imprinted (IIP) and Non-imprinted NIP cryogel polymers toward U(VI) were investigated in the presence of U(VI)-Nd(III), U(VI)-La(III) and U(VI)-Y(III) ion pairs. For this purpose 25 mL of 10 ppm lanthanide solutions in 10 mM phosphate buffer, pH 7.0 were passed from columns containing IIP and NIP at a flow rate of 1 mL/min at room temperature. Analysis of the lanthanide ions in the column output samples was performed by ICP-MS.

The distribution coefficient of U(VI) ion between the columns containing IIP and NIP and aqueous solutions was calculated using the following formula:

$$K_d = (C_i - C_f / C_f)(V/m) \quad (3)$$

where $K_d$ is the distribution coefficient, $C_i$ is initial U(VI) concentration and $C_f$ is final U(VI) concentration, V represents the solution volume (mL) and m is the polymer mass (g).

The selectivity coefficient (k) and relative selectivity coefficient ($k^1$) for U(VI) in the presence of other competing lanthanide ions can be calculated applying the following equation:

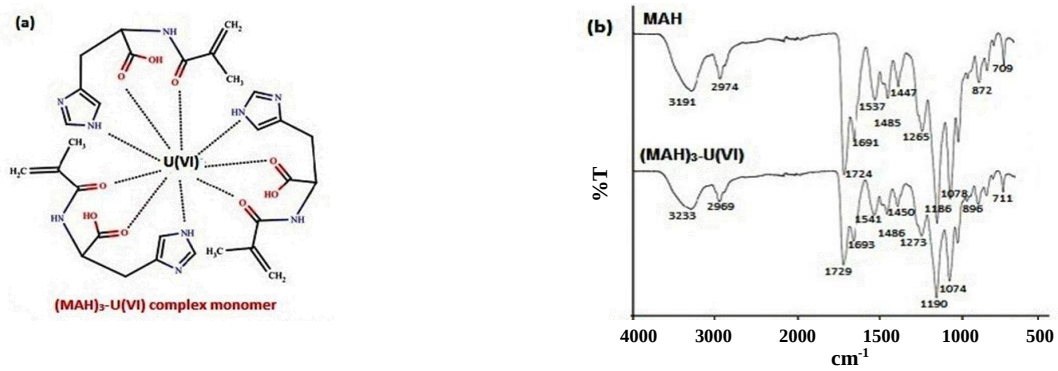


***Fig. 2: (a) Proposed structure for complex formed; (b) FT-IR spectrum for the MAH monomer and (MAH)₃U(VI) complex monomer.***

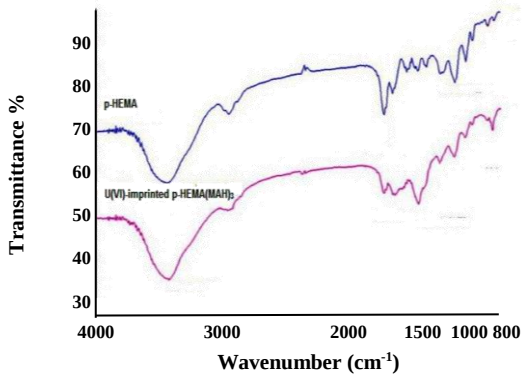


***Fig. 3: FT-IR Spectrum p-HEMA cryogel and U(VI)-imprinted p-HEMA-(MAH)₃ cryogel polymer.***

$$k = K_{(U(VI))} / K_{(interfering\ ion)} \quad (4)$$

$$k^{-1} = K_{(imprinted)} / K_{(nonimprinted)} \quad (5)$$

Where $K_{(U(VI))}$ is the distribution ratio of U(VI) ion and $K_{(interfering\ ion)}$ is the distribution ratio of potentially interfering ions.

### *Reusability of U(VI)-imprinted Cryogel Polymer (IIP)*

For the reusability studies, adsorption and desorption studies were repeated 10 times using same IIP. After each step, column was washed with 10 mL of 5 mol/L $HNO_3$ and deionized water.

### *Adsorption Studies of U(VI) ion from Soil Certified Reference Material*

Soil certified reference material was selected as the real sample for the selective adsorption of U(VI). For this purpose, 0.1 g soil certified reference material powdered was leached using concentrated $HNO_3$ and $H_2SO_4$ by microwave irradiation. Then, solution pH was adjusted to 7.0 using phosphate buffer and volume of the final solution was distilled to 100 mL by deionized water. The prepared solution was passed through the columns containing IIP and NIP the under the optimum conditions. Analysis of the ions in the column output samples was performed by ICP-MS.

## RESULTTS AND DISCUSSION

### *Characterization of MAH monomer and (MAH)₃U(VI) Complex Monomer*

Prepared $(MAH)_3$-U(VI) complex monomer were characterized by FT-IR spectroscopy, which proved that monomer and complex monomer were synthesized. The obtained FT-IR spectrum of the MAH monomer and $(MAH)_3U(VI)$ complex monomer is given in Fig. 2.

### *Characterization of U(VI)-Imprinted p-HEMA-(MAH)₃ Cryogel Polymer (IIP)*

p-HEMA and Th(IV)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer (IIP) were characterized by FT-IR and SEM. Fig. 3 shows the FT-IR Spectra p-HEMA and U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer. As can be seen, p-HEMA and U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer exhibited FT-IR patterns with small differences which confirms the similar polymer backbone.

The pore structure and pore size of U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer were visualized with SEM images as seen in Fig. 4. As shown in the Fig. 3, the U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel polymer has interconnected pores and porous structure. Pore size was found about 50 µm.

The equilibrium swelling degree and macroporosity of the U(VI)-imprinted p-HEMA-$(MAH)_3$ cryogel were 6.12 g $H_2O$/g cryogel and 81.04%, respectively.

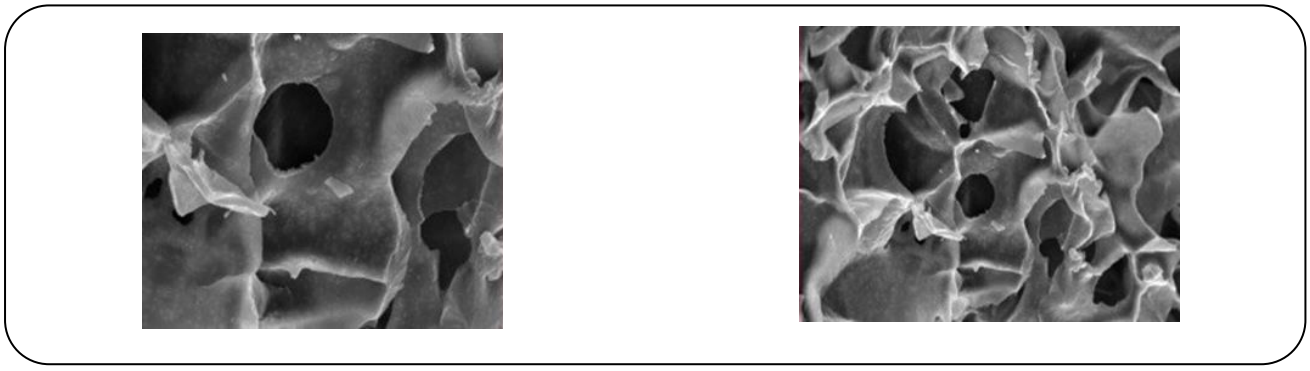

*Fig. 4: SEM images U(VI)-imprinted p-HEMA-(MAH)$_2$ cryogel polymer (IIP).*

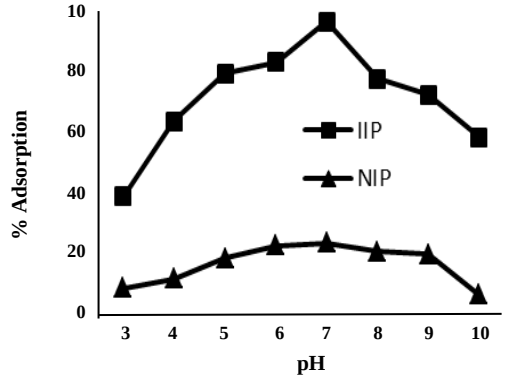


*Fig. 5: Effect of pH on U(VI) Adsorption [Experimental conditions: Initial U(VI) Concentration: 10 ppm; Temperature: 25 °C; Flow rate: 1 mL.min$^{-1}$; Time: 1 h.].*

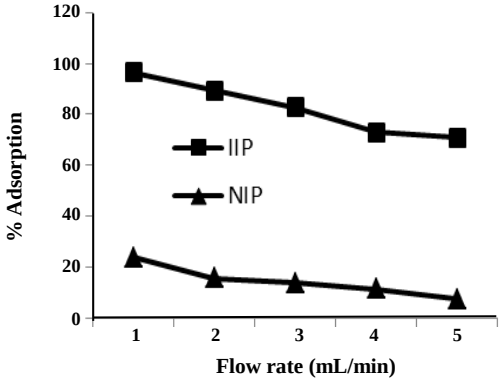


*Fig. 6: Effect of Flow Rate on U(VI) Adsorption [Experimental conditions: pH:5; Initial U(VI) Concentration: 10 ppm; Temperature: 25°C; Time: 1 h.].*

### *Adsorption Studies of U(VI) on IIP and NIP*

*pH effect on U(VI) Adsorption*

The change in amount of U(VI) adsorption to the IIP and NIP as a function of pH was investigated, as seen in Fig. 5. The maximum U(VI) binding to the IIP and NIP pH 7.0. This could be explained by electron transfer based covalent cross-linking between U(VI) and L-histidine of the functional monomer at pH 7.0. Fig. 5 clearly shows effect of pH on U(VI) binding to the IIP and NIP. As seen in the figure, the values higher and lower than pH 7.0 lead to low adsorption of U(VI) to the IIP and NIP, which can be explained by the repulsive electrostatic interactions between bound U(VI) ion and MAH monomer. The adsorption efficiency may decrease because of the size of conformation and the lateral electrostatic interactions between adjacent U(VI) ion on the IIP and NIP.

### *Flow Rate Effect on U(VI) Adsorption*

The flow rate of the U(VI) solution pumped through the cryogel is one of the crucial parameter for the control of binding process [46]. The flow rate effect on the adsorption of U(VI) was explored by changing the flow rate from 1.0 to 5.0 mL/min. 10 ppm U(VI) solution was used for this purpose. Owing to the back pressure produced by the column, the flow rates higher than 5.0 mL.min$^{-1}$ could not be investigated. As shown in Fig. 6, increasing flow rate resulted in a decrease in the adsorption of U(IV) from 96.56% to 70.84% adsorption capacity.

### *The Determination Maximum Adsorption Capacity of IIP and NIP*

Initial U(VI) concentration dependence of the bound amount of the U(VI) on to IIP and NIP is depicted in Fig. 7. As can be seen Fig. 7, U(VI) adsorption increased when initial U(VI) concentration is increased, and an equilibrium was obtained at a U(VI) concentration of 2000 ppm. The maximum adsorption capacity was obtained as 74.80 mg/g for IIP , while that of NIP was 14.76 mg/g. it was found that maximum adsorption

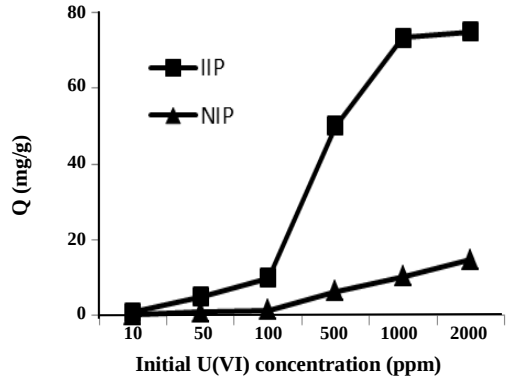


***Fig. 7: Effect of Initial U(VI) Concentration on Th(IV) Adsorption [Experimental conditions: pH:5; Temperature: 25°C; Flow rate: 1 mL.min$^{-1}$; Time: 1 h.].***

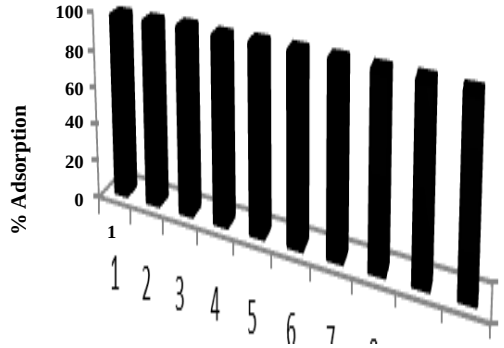


***Fig. 8: Reusability of IIP [Experimental conditions: pH:5; Initial U(VI) Concentration: 10 ppm; Temperature: 25°C; Flow rate: 1 mL.min$^{-1}$; Time: 1 h.].***

yield obtained was good result when compared to other studies [2, 3, 7].

***Regeneration and Reusability of the IIP***

One of the crucial advantage for an affinity material for the recognition and separation processes is its reusability [51]. To test the reusability of the prepared IIP, U(VI) adsorption and desorption cycle was repeated 10 times using the same cryogel (Fig. 8). The elution of U(VI) from the IIP was performed by using 10 mL 5.0 mol/L $HNO_3$ as the desorption solution and complete removal of U(VI) was achieved after the desorption step. It was found that the adsorption behavior of the IIP towards U(VI) did not changed significantly after ten adsorption and desorption cycles. Thus, one can easily say that the IIP are stable and the IIP can be used many times without significantly loss of their adsorption capacity.

***Selectivity Studies***

Competitive adsorption of U(VI)-Nd(III), U(VI)-La(III) and U(VI)-Y(III) were also explored in a column system. The obtained results are given in Table 1. U(VI) imprinted cryogel polymer (IIP) exhibited higher selectivity toward U(VI) ions over Nd(III), La(III) and Y(III) ions. $K_d$ values for the IIP were compared with NIP. The obtained results confirmed that the relative selectivity coefficients of the IIP for the U(VI)/Nd(III), U(VI)/La(III) and U(VI)/Y(III) were 129, 60 and 79 times higher than the corresponding NIP, respectively. As a result, it was found that the prepared U(VI)-imprinted cryogel polymer (IIP) exhibited a selectivity to U(VI) ion in the presence of other lanthanides.

***Selective Adsorption of U(VI) from Soil Certified Reference Material***

The outcomes of the adsorption of U(VI) from certified reference material are given in Fig. 9. The results showed that the IIP displayed 93.11% adsorption toward U(VI) while NIP showed 18,74.% adsorption.

**CONCLUSIONS**

We have shown that U(VI)-imprinted cryogel polymer (IIP) that contains Poly-Hydroxyethyl Methacrylate-Methacryloyl-L-Histidine is selective and has high adsorption capacity for U(VI) ion. A High adsorption rate was observed at the beginning of the adsorption process and saturation values are reached within 60 minutes. The maximum U(VI) adsorption capacity of the cryogel polymer was 74.80 mg/g for U(VI)-imprinted cryogel polymer, while that of non-imprinted cryogel polymer (NIP) was 14.76 mg/g. The adsorption amount of U(VI) was maximum at pH 7.0. Competitive adsorption studies showed that, U(VI)-imprinted p-HEMA(MAH)$_3$ are only selective to U(VI) ion, even in the presence of other lanthanide ions such as, Nd(III), La(III) and Y(III) ions. Distribution (Kd), selectivity (k), and relative selectivity (k′) coefficients were also calculated. The value of k′ was found, 129, 60, and 79 for Nd(III), La(III), and Y(III), respectively. These k′ values are high values if they are compared with reported research values. The obtained adsorption order under competitive conditions was U(VI) > La(III) >Y(III) >Nd(III). As a result, in our study to selectively remove the uranium used as fuel in nuclear reactors,

***Table 1. $K_d$, k and k' values of Nd(III), La(III) and Y(III) with respect to U(VI) [Experimental conditions: pH:5; Temperature: 25°C; Flow rate: 1 mL/min; Time: 1 h.]***

| Cryogel Column | U(VI) (ppm) | Nd(III) (ppm) | $K_d$ (U(IV)) | $K_d$ (Nd(III)) | *k* | *k'* |
|---|---|---|---|---|---|---|
| Non-imprinted | 10 | 10 | 761,2 | 1972,1 | 0.38 | - |
| U(IV)-imprinted | 10 | 10 | 98090 | 2760,1 | 35,5 | 129 |
| Cryogel Column | U(VI) (ppm) | La(III) (ppm) | $K_d$ (U(IV)) | $K_d$ (La(III)) | *k* | *k'* |
| Non-imprinted | 10 | 10 | 1827.9 | 2633,5 | 0.70 | - |
| U(IV)-imprinted | 10 | 10 | 108155 | 2086,0 | 51,3 | 60 |
| Cryogel Column | U(VI) (ppm) | Y(III) (ppm) | $K_d$ (U(IV)) | $K_d$ (Y(III)) | *k* | *k'* |
| Non-imprinted | 10 | 10 | 927,8 | 2331.5 | 0.40 | - |
| U(IV)-imprinted | 10 | 10 | 73258 | 2041,0 | 36.0 | 79 |

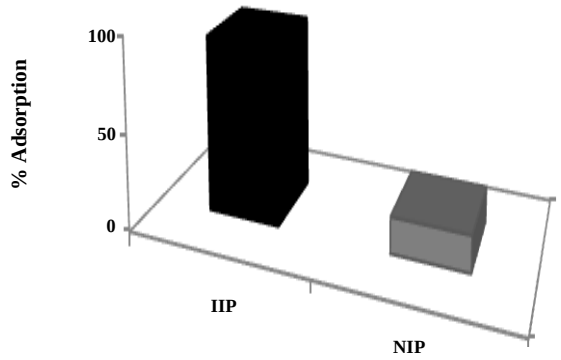


***Fig. 9: Selective adsorption of U(VI) from certified reference material [Experimental Conditions: $C_{U(VI)}$= 0.93 ppm (in the SRM), pH= 5.0, Flow Rate= 1 mL/min, T= 25°C].***

it was determined that the prepared uranium-imprinted polymer exhibited effective uranium bonding activity and thus selectively separated from the matrix environment where uranium was found. After this stage, it is advisable to use sustainable membranes to purify the separated uranium and make it ready for use in the reactors [52].

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## REFERENCES

[1] Wang J., Chen Z., Shao D., Li Y., Xu Z., Cheng C, Asiri A.M., Marwani H.M., Hu S., Adsorption of U(VI) on Bentonite in Simulation Environmental conditions, *Journal of Molecular Liquids*, **242:** 678–684 (2017).

[2] Iliaa R., Liatsou I., Savva I., Vasile E., Vekas L., Marinica, O., Mpekris F., Pashalidis I., Christoforou T.K., Magnetoresponsive Polymer Networks as Adsorbents for the Removal of U(VI) Ions from Aqueous Media, *European Polymer Journal*, **97**: 138-146 (2017).

[3] Li F., Yang Z., Weng H., Chen G., Lin M., Zhao C., High Efficient Separation of U(VI) and Th(IV) from Rare Earth Elements in Strong Acidic Solution by Selective Sorption on Phenanthroline Diamide Functionalized Graphene Oxide, *Chemical Engineering Journal*, **332:** 340-350 (2018).

[4] Wang Y.L., Huang C., Li F.J., Dong Y.M., Sun X.Q., Process for the Separation of Thorium and Rare Earth Elements from Radioactive Waste Residues Using Cyanex® 572 as a New Extractant, *Hydrometallurgy*, **169:** 158–164 (2017).

[5] Lu Y., Wei H., Zhang Z., Li Y., Wu G., Liao W., Selective Extraction and Separation of Thorium from Rare Earths by a Phosphorodiamidate Extractant, *Hydrometallurgy*, **163:** 192–197 (2016) .

[6] Wang Y., Wu L., Yang Y., Feng W., Yuan L., Efficient Separation of Thorium from Rare Earths with a Hydrogen-Bonded Oligoaramide Extractant in Highly Acidic Media, *Journal of Radioanalytical Nuclear Chemistry*, **305:** 543–549 (2015) .

[7] Zhu Z., Pranolo Y., Cheng C.Y., Separation of Uranium and Thorium from Rare Earths for Rare Earth Production - A Review, *Mineral Engineering*, **77:** 185–196 (2015).

[8] Gu Z., Probing the Problems of Thorium Utilization as a Nuclear Energy Resource, *Chinese Journal of Nuclear Science and Engineering*, **27**: 97–105 (2007).

[9] Abdollahy M., Shojaosadati S.A., Tavakoli H.Z., Valivand A., Bioleaching of Low Grade Uranium Ore of Saghand Mine, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **10:** 71-79 (2011).

[10] Chmielewski A.G., Nuclear Fissile Fuels Worldwide Reserves, *Nukleonika*, **53:** 11–14 (2008).

[11] Horwitz E.P., Dietz M.L., Chiarizia R., Diamond H., Essling A.M., Graczyk M., Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography, *Analytica Chimica Acta*, **266**: 25-37 (1992).

[12] Dolak I., Karakaplan M., Ziyadanogulları B., Ziyadanogulları R., Solvent Extraction, Preconcentration and Determination of Thorium with Monoaza 18-Crown-6 Derivative, *Bulletin of the Korean Chemical Society*, **32:** 1564-1568 (2011).

[13] Yener I., Oral E.V., Dolak I., Ozdemir O., Ziyadanogulları R., A New Method for Preconcentration of Th (IV) and Ce (III) by Thermophilic Anoxybacillus Flavithermus Immobilized on Amberlite XAD-16 Resin as a Novel Biosorbent, *Ecological Engineering*, **103**: 43-49 (2017).

[14] Kaminski M.D., Nunez L., Separation of Uranium from Nitric- and Hydrochloric-acid Solutions with Extractant-Coated Magnetic Microparticles, *Separation Science and Technology*, **35**: 2003-2018 (2000).

[15] Haerizade B.N., Ghavami M., Koohi M., Darzi S.J., Rezaee N., Kasaei M.Z., Green Removal of Toxic Pb(II) from Water by a Novel and Recyclable Ag/γ-Fe2O3@r-GO Nanocomposite, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **37:** 29-37 (2018).

[16] Dolak I., Tegin I., Guzel R., Ziyadanogulları R., Removal and Preconcentration of Pb(II), Cr(III), Cr(VI) from the Aqueous Solution and Speciation of Cr(III)-Cr(VI)- by Using Functionalized Amberlite XAD-16 Resin with Dithioethylenediamine, *Asian Journal of Chemistry*, **22:** 6117-6124 (2010).

[17] İnam R., Çaykara T., Özyürek C., Polarographic Determination of Uranyl Ion Adsorption on Poly-(2-Hydroxyethyl Methacrylate/itaconic acid) Hydrogels, *Separation Science and Technology*, **36**: 1451-1461 (2001).

[18] Sana S., Roostaazad R., Yaghmaei S., Biosorption of Uranium (VI) from Aqueous Solution by Pretreated Aspergillus niger Using Sodium Hydroxide, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **8**: 65-74 (2015).

[19] Dolak I., Keçili R., Hür D., Ersöz A., Say R., Ion-Imprinted Polymers for Selective Recognition of Neodymium (III) in Environmental Samples, *Industrial & Engineering Chemistry Research*, **54**: 5328-5335 (2015).

[20] Keçili R., Dolak I., Ziyadanoğulları B., Ersöz A., Say R., Ion Imprinted Cryogel-Based Supermacroporous Trapsfor Selective Separation of Cerium (III)in Real Samples, *Journal of Rare Earths*, **36**: 857-862 (2018).

[21] Dolak I., Selective Separation and Preconcenration of Thorium (IV) in Bastnaesite Ore Using Thorium (IV)-Imprinted Cryogel Polymer, *Hacettepe Journal of Biology and Chemistry*, **46**: 187-197 (2018).

[22] Harkins D.A., Schweitzer G.K., Preparation of Site-Selective Ion-Exchange Resins, *Separation Science and Technology*, **26**: 345-354 (1991).

[23] Panahi H.A., Zadeh M.S., Tavangari S., Moniri E., Ghassemi J., Nickel Adsorption from Environmental Samples by Ion Imprinted Aniline -Formaldehyde Polymer, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **31**: 35-44 (2012).

[24] Wulff G., Molecular Imprinting in Cross-Linked Materials with the Aid of Molecular Templates—a Way Towards Artificial Antibodies, *Angewandte Chemie International Edition*, **34:** 1812-1832 (1995).

[25] Pakdehi S.G., Adsorptive Removal of Al, Zn, Fe, Cr and Pb from Hydrogen Peroxide Solution by IR-120 Cation Exchange Resin, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **11**: 75-84 (2016).

[26] Dhal P.K., Arnold F.H., Metal-Coordination Interactions in the Template-Mediated Synthesis of Substrate-Selective Polymers: Recognition of Bis(imidazole) Substrates by Copper(II) Iminodiacetate Containing Polymers, *Macromolecules*, **25:** 7051-7059 (1992).

[27] Chen F., Yang Z., Tang Y., Wang X., Selective Extraction and Determination of Di(2-ethylhexyl) Phthalate in Aqueous Solution by HPLC Coupled with Molecularly Imprinted Solid-phase Extraction, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **36**: 127-136 (2017).

[28] Didaskalou C., Buyuktiryaki S., Kecili R., Fonte C.P., Szekely G., Valorisation of Agricultural Waste with an Adsorption/Nanofiltration Hybrid Process: from Materials to Sustainable Process Design, *Green Chemistry*, **19**: 3116-3125 (2017).

[29] Székely G., Fritz E., Bandarra J., Heggie W., Sellergren B., Removal of Potentially Genotoxic Acetamide and Arylsulfonate Impurities from Crude Drugs by Molecular Imprinting, *Journal of Chromatography A*, **1240**: 52-58 (2012).

[30] Dolak I., Keçili R., Onat R., Ziyadanoğulları B., Ersöz A., Say R., Molecularly Imprinted Affinity Cryogels for the Selective Recognition of Myoglobin in Blood Serum, *Journal of Molecular Structure*, **1174:** 171-176 (2018).

[31] Székely G., Bandarra J., Heggie W., Sellergren B., Ferreira F.C., A Hybrid Approach to Reach Stringent Low Genotoxic Impurity Contents in Active Pharmaceutical Ingredients: Combining Molecularly Imprinted Polymers and Organic Solvent Nanofiltration for Removal of 1,3-Diisopropylurea, *Separation and Purification Technology*, **86**: 79-87 (2012).

[32] Saylan Y., Yilmaz F., Özgür E., Derazshamshir A., Yavuz H., Denizli A., Molecular Imprinting of Macromolecules for Sensor Applications, *Sensors*, **17:** 1-30 (2017).

[33] Sellergren B., Imprinted Chiral Stationary Phases in High-Performance Liquid Chromatography, *Journal of Chromatofraphy A*, **906**: 227-252 (2001).

[34] Wei S., Mizaikoff B., Recent Advances on Noncovalent Molecular Imprints for Affinity Separations, *Journal of Separation Science*, **30**: 1794-1805 (2007).

[35] Vedadghavami A., Minoei F., Hosseini S.S., Practical Techniques for Improving Teh Performance of Polymeric Membranes and Processes for Protein Separation and Purification, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **37**: 1-23 (2018).

[36] Lasáková M., Jandera P., Molecularly Imprinted Polymers and Their Application in Solid Phase extraction, *Journal of Separation Science*, **32:** 788-812 (2009).

[37] Alvarez-Lorenzo C., Concheiro A., Molecularly Imprinted Polymers for Drug Delivery, *Journal of Chromatography B*, **804:** 231-245 (2004).

[38] Vidyasankar S., Arnold F.H., Molecular Imprinting: Selective Materials for Separations, Sensors and Catalysis, *Current Opinial Biotechnology*, **6:** 218-224 (1995).

[39] Monier M., Abdel-Latif D.A., Fabrication of Au(III) Ion-Imprinted Polymer Based on Thiol-Modified Chitosan, *International Journal of Biological Macromolecules*, **105**: 777-787 (2017).

[40] Moussa M., Pichon V., Mariet C., Vercouter T., Delaunay N., Potential of Ion Imprinted Polymers Synthesized by Trapping Approach for Selective Solid Phase Extraction of Lanthanides, *Talanta*, **161:** 459-468 (2016).

[41] Moorthy M.S., Tapaswi P.K., Park S.S., Mathew A., Cho H.-J., Ha C.-S., On-imprinted Mesoporous Silica Hybrids for Selective Recognition of Target Metal Ions, *Microporous and Mesoporous Materials*, **180:** 162-171 (2013).

[42] Monier M., Abdel-Latif D.A., Abou El-Reash Y.G., Ion-Imprinted Modified Chitosan Resin for Selective Removal of Pd(II) Ions, *Journal of Colloidal and Interface Science*, **469**: 344-354 (2016).

[43] Mitreva M., Dakova I., Karadjova I., Iron(II) Ion Imprinted Polymer for Fe(II)/Fe(III) Speciation in Wine, *Microchemica Journal*, **132**: 238-244 (2017).

[44] Msaadi R., Ammar S., Chehimi M.M., Yagci Y., Diazonium-Based Ion-Imprinted Polymer/Clay Nanocomposite for the Selective Extraction of Lead(II) Ions in Aqueous Media, *European Polymer Journal*, **89:** 367-380 (2017).

[45] Roushani M., Abbasi S., Khani H., Sahraei R., Synthesis and Application of Ion-Imprinted Polymer Nanoparticles for the Extraction and Preconcentration of Zinc Ions, *Food Chemistry*, **173**: 266-273 (2015).

[46] Fayazi M., Ghanei M.M., Taher M.A., Ghanei-Motlagh R., Salavati M.R., Synthesis and Application of a Novel Nanostructured Ion-Imprinted Polymer for the Preconcentration and Determination of Thallium(I) Ions in Water Samples, *Journal of Hazardous Materials*, **309**: 27-36 (2016).

[47] Candan N., Tüzmen N., Andaç M., Andaç C.A., Say R., Denizli A., Cadmium Removal out of Human Plasma Using Ion-Imprinted Beads in a Magnetic Column, *Materials Science and Engineering C*, **29**: 144-152 (2009).

[48] Gao B., Meng J., Xu Y., Zhang Y., Preparation of Fe(III) Ion Surface-Imprinted Material for Removing Fe(III) Impurity from Lanthanide Ion Solutions, *Journal of Industrial Engineering and Chemistry*, **24**: 351-358 (2015).

[49] Bereli N., Saylan Y., Uzun L., Say R., Denizli A., L-Histidine Imprinted Supermacroporous Cryogels for Protein Recognition, *Separation and Purification Technology*, **82**: 28-35 (2011).

[50] Baysal Z., Aksoy E., Dolak I., Ersöz A., Say R., Adsorption Behaviours of Lysozyme onto Poly-Hydroxyethyl Methacrylate Cryogels Containing Methacryloyl Antipyrine-Ce(III), *International Journal of Polymeric Materials and Polymeric Biomaterials*, **67**: 199-204 (2018).

[51] Kupai J., Razali M., Buyuktiryaki S., Kecili R., Szekely G., Long-Term Stability and Reusability of Molecularly Imprinted Polymers, *Polymer Chemistry*, **8**: 666-673 (2017).

[52] Fodi T., Didaskalou C., Kupai J., Balogh G.T., Huszthy P., Szekely G., Nanofiltration-Enabled In Situ Solvent and Reagent Recycle for Sustainable Continuous-Flow Synthesis, *Chem Sus Chem*, **10:** 3435-3444 (2017).