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ARTICLE

Synthesis of highly dense and selective imprinted polymer via pre-irradiated surface-initiated graft polymerization†

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A new surface ion-imprinted polymer for the selective sorption of U(VI) was prepared by a pre-irradiated surface-initiated graft polymerization in the presence of U(VI)-methacrylic acid complex. Pre-irradiation in air is a green, convenient, effective and low-cost approach for immobilization of the peroxide and hydroperoxide as initiator on the surface. Moreover, U(VI) can promote the decomposition of peroxide and hydroperoxide to the oxy radicals to induce graft polymerization. The adsorption behavior of U(VI) onto the imprinted polymer was investigated as functions of pH, contact time, temperature and initial U(VI) concentration by batch experiments. The selectivity study revealed that the U(VI)-imprinted polymer exhibited excellent selectivity and good affinity to U(VI) in the presence of competitive metal ions.

1. Introduction

Uranium is the most important element for nuclear industry. The inhalation of uranium results in progressive or irreversible renal injury and in acute cases may lead to kidney failure and death due to its natural radioactivity and chemical toxicity.¹ Therefore, the selective removal and recovery of uranium from environmental samples has attracted more and more attention. So far, various separation and preconcentration techniques, such as chemical precipitation,^{2,3} liquid-liquid extraction,⁴⁻⁶ ion exchange^{7,8} and solid phase extraction (SPE)⁹⁻¹⁴ have been employed for the removal of uranium(VI). Among these methods, SPE appears to be a particularly effective method because of its simplicity, flexibility, low cost, absence of emulsion and higher enrichment factor.¹⁵ The ion imprinted polymer (IIP) is a promising SPE sorbent in selective separation and preconcentration of uranium(VI) due to its high selectivity and good affinity for the target ion.

The IIP is generally prepared by copolymerization of functional monomer and cross-linker in the presence of the template ion. Bulk polymerization is the most commonly used imprinting technique. However, IIP prepared by this method has been encountered with various limitations such as incomplete template removal, slow mass transfer and inaccessible binding sites situated deeply inside the bulk of the polymer matrix.¹⁶⁻¹⁸ In order to overcome these problems, the surface ion-imprinting technique where the sites are situated

at the surface or in the proximity of substrates surface is developed, providing the complete removal of templates, low mass-transfer resistance and good accessibility to the target species.^{1,19,20}

The “grafting to” and “grafting from” methods are mainly used to graft polymer chains on the surface of supporting material for preparation of surface imprinted polymers.^{16,21} In the “grafting to” method, the living polymer chains are reacted with the functional groups on the surface. A low grafting density is obtained by this method due to the steric restriction.^{22,23} The “grafting from” method where the polymer chains are initiated from the surface-attached initiators followed by in situ polymerization is preferred for graft polymerization since it's easy to control the grafting density. In this method, the free radicals formed by the decomposition of the initiators introduced onto the surface are situated at the surface or in the proximity of the surface. As a result, the polymer chains propagate mainly on the surface and a high polymer grafting density was obtained compared with the “grafting to” method.^{16,24} In the ion imprinting technology, a dense and rigid polymer structure which leads to a high selectivity is expected to be obtained via a “grafting from” polymerization. To coat the surface of the substrate with imprinted polymers by a “grafting from” method is most commonly done by the chemical immobilization of azo-initiator or atom transfer radical polymerization (ATRP) initiator on the surface, followed by initiating a polymerization reaction of monomers.^{16,20} However, the surface immobilization of initiator remains complex and difficult because of their chemical instability.¹⁷ Moreover, ATRP is not suitable for ion imprinting technology due to the presence of Cu²⁺. Pre-irradiation in air at room temperature is a green, convenient, effective and low-cost method to introduce peroxide and hydroperoxide onto the surface of the substrate.²⁵⁻²⁷ The introduced peroxide and hydroperoxide are

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stable at room temperature. The oxy radicals can subsequently be formed by the decomposition of the peroxide and hydroperoxide at an elevated temperature to induce graft polymerization.

Various U(VI) imprinted polymers have been successfully prepared with carboxylic acid functional monomers due to its strong tendency toward U(VI) according to hard-hard interaction concept.^{16,28-30} In this study, the U(VI) surface imprinted polymers was prepared via a pre-irradiated surface graft polymerization. To the best of our knowledge, there is no previous report on the use of this method in combination with surface imprinting technique. The IIP was prepared by copolymerization of methacrylic acid-U(VI) complex with cross-linker onto pre-irradiated amino groups functionalized silica particles. The characterization of the synthesized polymeric sorbent and adsorption of U(VI) on sorbent are described and discussed.

2. Experimental

2.1 Chemicals and reagents

3-Aminopropyltriethoxysilane (APTES), ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), 5,7-dichloro-8-quinolinol (DCQ) and pyridine were purchased from Aldrich. silica gel (300-400 mesh) (Aladdin) was used as received. All other chemical reagents were of the analytical reagent grade. Milli-Q water was used in all experiments.

2.2 Synthesis of amino groups functionalized silica particles

Amino groups functionalized silica particles (Si-NH₂) were synthesized according to the method reported in literature.¹⁷ Briefly, 5 g of activated silica gel and 1.5 mL of APTES were added into 50 mL of anhydrous toluene. The mixture was refluxed for 12 h under dry nitrogen. The resultant particles were dried at 120 °C for 3h after washed several times with toluene and ethanol.

2.3 Synthesis of U(VI)-imprinted Polymer (IIP) and non-imprinted polymer (NIP)

Si-NH₂ was irradiated by γ -ray from a ⁶⁰Co source in air at room temperature with a dose of 75kGy and dose rate of 4.5 kGy/h. The U(VI)-imprinted polymer was prepared by thermal polymerization. Typically, 0.5mmol of UO₂(NO₃)₂•6H₂O was slowly added to 25mL of 2-methoxyethanol containing 1mmol of methacrylic acid with continuous stirring. After the mixture was stirred for 3 h at room temperature, 4 mmol of EGDMA and 0.75 g of pre-irradiated Si-NH₂ were added. The above solution was purged with nitrogen for 15 min to remove oxygen while cooled in ice bath. Then, the mixture was stirred and heated at 60 °C under nitrogen atmosphere for 24 h. The product was obtained by filtration, washed with acetone and deionized water. Finally, U(VI) were leached by 3 M HCl solution repeatedly until no U(VI) in the filtrate was detected. The final product was cleaned with deionized water and dried in a vacuum oven at 70 °C for 12 h. The non-imprinted polymer (NIP) was also prepared using a similar procedure in the

absence of U(VI). The recipe of the copolymerization was changed to synthesize the IIP and NIP with different composition (Table 1).

Table 1 Synthesis of IIP and NIP.

Sample	U(VI) (mmol)	DCQ (mmol)	Pyridine (mmol)	FeSO ₄ (mmol)
IIP1	0.5	0	0	0
IIP2	0.5	1	1	0
NIP1	0	0	0	0
NIP2	0	0	0	0.5

2.4 Characterization

The concentrations of metal ions were analyzed by ICP-AES (PerkinElmer, USA). FT-IR measurements were performed using the Nicolet iN 10 FT-IR spectrometer (Thermo-Fischer, USA) over a range from 400 to 4000 cm⁻¹. The Barrett-Emmett-Teller (BET) surface area was measured by N₂ adsorption isotherm using an ASAP 2010 Micromeritics instrument. The surface morphology of the polymer particles was examined by scanning electron microscope (LEO 1530VP, USA). Thermo-gravimetric analysis was performed using a thermal analysis instrument (SSC/5200 SII, Seiko, Japan), at N₂ atmosphere, from room temperature to 800 °C at a heating rate of 10 °C min⁻¹.

2.5 Batch sorption experiments

Batch experiments were performed to study the adsorption behaviour of IIP toward U(VI). 60 mg U(VI)-imprinted polymer was added to 10 mL metal ions solution after adjusting to the desired pH value. After the mixture was shaken for 3h, the solution was centrifuged and the concentration of the metal ion in the solution was determined by ICP-AES. The distribution coefficient K (mL g⁻¹), the adsorption capacity Q (mg g⁻¹), the percentage of metal ion adsorbed on the sorbent %uptake, the selectivity coefficient $S_{U/M}$ were calculated as the following equations:

$$K = \frac{(C_0 - C_e)V}{C_e W} \quad (1)$$

$$Q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

$$\% \text{uptake} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

$$S_{U/M} = \frac{K_U}{K_M} \quad (4)$$

Where C_0 and C_e represented the initial and equilibrium concentration (mg L⁻¹), respectively, V was the volume of solution (L) and W was the mass of the sorbent (g).

3. Results and discussion

3.1 Synthesis and characterization of imprinted polymer

The process for preparation of U(VI)-imprinted polymer was described in Scheme 1. In the first step, amino groups were introduced to the surface of silica particles by silylated reaction with APTES. The resultant Si-NH₂ was irradiated in air at room temperature to introduce the hydroperoxide and

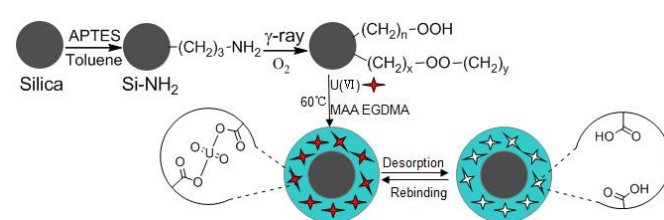
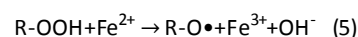
peroxide onto the surface of the substrate. Then, the pre-irradiated Si-NH₂ was added into the polymerization solution containing template ion (U(VI)), functional monomer (MAA), cross linker (EGDMA). The graft polymerization was initiated by the oxy radicals formed by the decomposition of the peroxide and hydroperoxide at an elevated temperature. Finally, U(VI) were leached by HCl solution. The FT-IR spectra of the Si-NH₂ and IIP1 are shown in Fig. 1A. The spectra of the Si-NH₂ showed an absorption peak around 1100 cm⁻¹ attributed to the asymmetric vibration of Si-O-Si group, while the peaks around 798 and 467 cm⁻¹ were assigned to Si-O-Si symmetric and bending vibration, respectively.¹⁸ Compared with Si-NH₂, the FT-IR spectra of IIP1 displayed a new characteristic peak around 1737 cm⁻¹ attributed to stretching vibration of C=O group of EGDMA.¹⁴ Fig. 1C and 1D show the SEM images of silica and IIP1. Compared with silica, IIP1 showed a porous surface, which could be attributed to the surface initiated imprinting process. TGA curves of the Si-NH₂ and IIP1 are shown in Fig. 1B. IIP1 displayed a dramatically high weight loss compared to Si-NH₂ due to the imprinted polymer grafted onto the surface. The estimated BET surface area of leached and unleached IIP1 was found to be 297.9 m² g⁻¹ and 264.1 m² g⁻¹, respectively (Table 2). The higher surface area of leached IIP1 may be attributed to the elution of U(VI). Moreover, a BJH average pore diameter of 3.3 nm during adsorption indicated the prominent mesoporous nature of IIP1. The N₂ adsorption-desorption isotherms and pore size distribution curves of leached and unleached IIP1 are displayed in Fig. S1. It could be found that the pore size was relatively uniform. Meanwhile, the different pore size distribution of leached and unleached IIP1 may be attributed to the pores of smaller size formed by elution of U(VI). All these results confirmed that the imprinted polymer layer was successfully grafted onto the surface of silica particles.

Table 2 N₂ adsorption data for leached and unleached IIP1.

	leached IIP1	unleached IIP1
BET surface area (m ² g ⁻¹)	297.9	264.1
Total pore volume (mL g ⁻¹)	0.237	0.274
Average pore diameter (nm)	3.3	9.2

The IIP1 was successfully prepared via surface graft polymerization at 60 °C. Unfortunately, the synthesis of NIP1 using an identical procedure as that of IIP1 in the absence of U(VI) was unsuccessful, which was confirmed by the absence of the absorption peak around 1737 cm⁻¹ in the FT-IR spectra (Fig. 1A) and the almost same weight loss with Si-NH₂(Fig. 1B). Thus, we concluded that U(VI) is crucial to graft of polymer onto the surface. Considering that Fe²⁺ could promote the decomposition of the hydroperoxide to oxy radicals by redox as Eqs. 5,³¹ NIP2 was prepared in the presence of Fe²⁺. The resultant exhibited an absorption peak around 1737 cm⁻¹(Fig. 1A) and a higher weight loss than Si-NH₂(Fig. 1B), which indicated that the polymer layer was successfully grafted onto the surface. Similarly, it could be deduced that U(VI) could promote the decomposition of the peroxide and

hydroperoxide to oxy radicals to induce the “grafting from” polymerization in the synthesis of IIP1. Moreover, the peroxide and hydroperoxide were generally decomposed at 80 °C or higher temperature.^{25,26} However, 60 °C was enough for decomposition of the peroxide and hydroperoxide in the synthesis of IIP1, which revealed the U(VI) promoted decomposition as well. A proposed mechanism for U(VI) promoted decomposition of the peroxide and hydroperoxide is shown in Scheme 2. The O-O bond of peroxide and hydroperoxide could be activated by U(VI) through the coordination of U(VI) with the peroxide and hydroperoxide, resulting in the decomposition of the peroxide and hydroperoxide. In order to verify the proposed mechanism, IIP2 was prepared in the presence of DCQ and pyridine which possess strong tendency toward U(VI). An almost same weight loss with Si-NH₂(Fig. 1B) and the absence of the absorption peak around 1737 cm⁻¹(Fig. 1A) indicated the unsuccessful graft of imprinted polymer onto the surface of silica substrate. In the synthesis of IIP2, a ternary complex of U(VI) with DCQ and pyridine was initially formed as shown in Scheme 3, which inhibited the further coordination of U(VI) with the peroxide and hydroperoxide. Therefore, the O-O bond couldn't be activated and the decomposition of peroxide and hydroperoxide did not occur. Consequently, the synthesis of IIP2 was frustrated.



Scheme 1 Scheme for the preparation of U(VI)-IIP by a pre-irradiated graft polymerization.

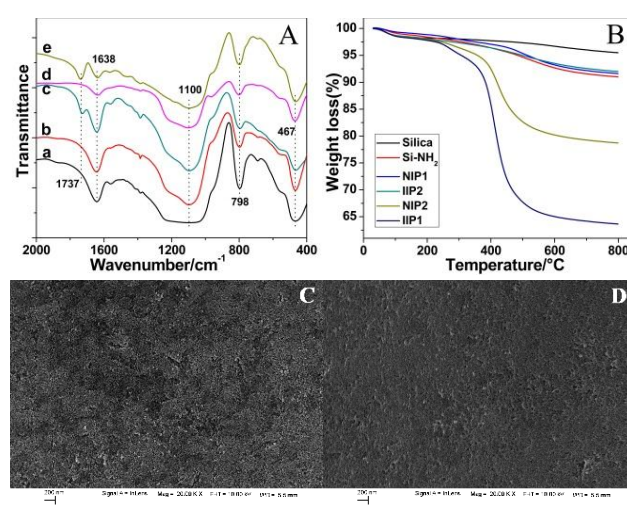
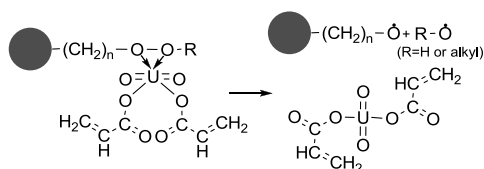
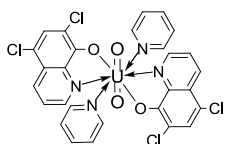


Fig. 1 (A) FT-IR spectra of Si-NH₂ (a), NIP1 (b), NIP2 (c), IIP2 (d) and IIP1 (e). (B) TGA curves of silica, Si-NH₂, NIP1, NIP2, IIP2 and IIP1. (C) SEM image of silica. (D) SEM image of IIP1.



Scheme 2 Scheme for U(VI) promoted decomposition of the peroxide and hydroperoxide.



Scheme 3 Scheme for ternary complex of U(VI) with DCQ and pyridine.

3.2 Adsorption study

3.2.1 Effect of pH. It is known that pH is an important parameter affecting the adsorption of metal ion. The effect of pH on the U(VI) uptake was investigated over pH values ranging from 2 to 6 by batch experiments. As shown in Fig. 2, the percent uptake of U(VI) ions increased with increasing pH from 2 to 4, and increased slightly in pH from 4 to 6. In order to obtain the maximum extraction efficiency, pH 5 was selected for subsequent studies.

3.2.2 Adsorption kinetics. The effect of adsorption time was investigated from 5 to 180 min and the result was shown in Fig. 3. The adsorption rate was initially fast and more than 95% uptake of U(VI) was achieved within 40 min.

In order to investigate the mechanism of the adsorption kinetics, the pseudo-first order and pseudo-second order kinetic models were employed to evaluate the obtained kinetic data. The two models can be expressed as linear form by Eqs. 6 and 7, respectively.³²

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

Where Q_e (mg g^{-1}) and Q_t (mg g^{-1}) are the amount of metal ion adsorbed at equilibrium and time t (min), respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first order and pseudo-second order rate constants of adsorption, respectively. For Eqs. 6 and 7, linear plots are shown in Fig. S2.

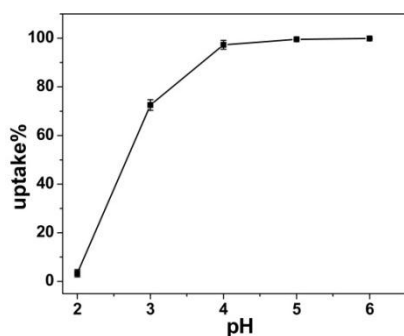


Fig. 2 Effect of pH on the uptake of U(VI) on IIP ($C_0 = 5 \text{ mg L}^{-1}$, $t = 3 \text{ h}$, $W = 60 \text{ mg}$, $V = 10 \text{ mL}$, and $T = 298.15 \text{ K}$).

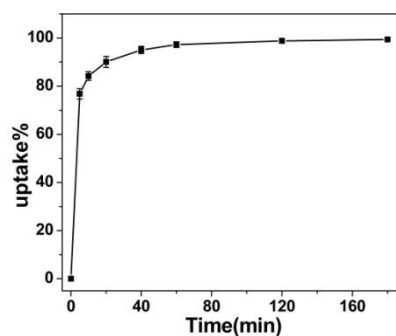


Fig. 3 Effect of contact time on the uptake of U(VI) on IIP ($C_0 = 5 \text{ mg L}^{-1}$, $\text{pH} = 5.0$, $W = 60 \text{ mg}$, $V = 10 \text{ mL}$, and $T = 298.15 \text{ K}$).

The kinetic parameters of two models are listed in Table S1. It can be observed that the correlation coefficient (R^2) of the pseudo-second order kinetic model (0.9999) is much higher than that of the pseudo-first order kinetic model (0.8961), indicating that the pseudo-second order kinetic model was a more appropriate model for describing the experimental adsorption data. These results suggested that the chemical adsorption step might be the rate-controlling step.³³

3.2.3 Effect of temperature. The effect of temperature on the uptake of U(VI) ion was investigated in the temperature range of 25–45 °C and the result revealed that the adsorption amount of U(VI) increased with increasing temperature. The thermodynamic parameters such as enthalpy change ΔH (kJ mol^{-1}) and entropy change ΔS ($\text{J mol}^{-1} \text{K}^{-1}$) were calculated from a linear plot of $\ln K_d$ versus $1000/T$ (Fig. S3) using Eq. 8 and Gibbs free energy change ΔG (kJ mol^{-1}) was calculated from Eq. 9.³⁴ The obtained thermodynamic parameters were listed in Table 3.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), K_d (L g^{-1}) is the equilibrium constant.

From the thermodynamic parameters in Table 3, the positive value of ΔH and the negative value of ΔG indicated that the uptake of U(VI) onto IIP was endothermic and spontaneous in nature. The positive value of ΔS showed the increased randomness at the solid-solution interface during the adsorption process.

Table 3 The thermodynamic parameters for the U(VI) adsorption onto IIP.

ΔH (kJ mol^{-1})	ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔG (kJ mol^{-1})
		298.15K
52.97	186.77	-2.71

3.2.4 Adsorption isotherm. The adsorption isotherm was used to evaluate the adsorption capacity of IIP for U(VI) by batch experiments in the initial concentration range of 5 to 100 mg L^{-1} . As can be seen in Fig. 4, the amount of U(VI) adsorbed per unit mass of IIP increased with increasing equilibrium concentration of U(VI).

The Langmuir and Freundlich isotherm models were often employed to fit the experimental data, which is important for understanding the mechanism of the adsorption. The linear forms

of the two models can be expressed by Eqs. 10 and 11, respectively.^{35,36}

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (10)$$

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (11)$$

Where C_e is the equilibrium concentration of the U(VI) ion (mg L^{-1}), Q_e is the equilibrium adsorption capacity (mg g^{-1}), Q_m is the maximum adsorption capacity (mg g^{-1}), K_L is the Langmuir binding constant related to the energy of adsorption (L mg^{-1}), K_F is Freundlich constant and n is the constant related to adsorption intensity. For Eqs. 10 and 11, linear plots are shown in Fig. S4.

The isotherm parameters of two models were given in Table 4. It was obvious from the correlation coefficient value (R^2) that the Langmuir model fitted the experimental data better than the Freundlich model, which indicated the monolayer adsorption of the U(VI) onto the homogeneous surface of IIP.^{36,37} The maximum adsorption capacity calculated was 46.42 mg g^{-1} .

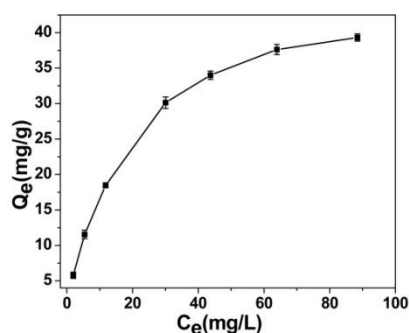


Fig. 4 Adsorption isotherm for adsorption of U(VI) onto IIP ($t = 3 \text{ h}$, $\text{pH} = 5.0$, $W = 10 \text{ mg}$, $V = 20 \text{ mL}$, and $T = 298.15 \text{ K}$).

Table 4 The Langmuir and Freundlich isotherm parameters for sorption of U(VI) by IIP.

Langmuir model		Freundlich model			
$K_L (\text{L g}^{-1})$	$Q_m (\text{mg g}^{-1})$	R^2	k_F	n	R^2
0.0632	46.42	0.998	4.71	1.965	0.971

3.2.5 Adsorption of U(VI) in low concentration. IIP was generally used for the selective separation and preconcentration of U(VI) from environmental and other low concentration samples. Thus, the performance of IIP on the sorption of U(VI) in low uranium concentration was evaluated by batch experiments. As shown in Fig. 5, IIP showed a high adsorption efficiency of U(VI) in low concentration, indicating good affinity of IIP towards U(VI).

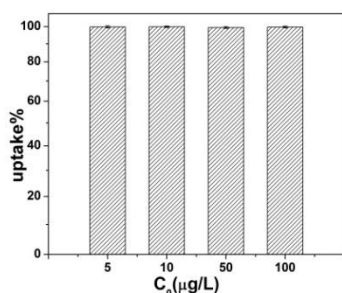


Fig. 5 Sorption of U(VI) in low uranium concentration ($t = 3 \text{ h}$, $\text{pH} = 5.0$, $W = 60 \text{ mg}$, $V = 10 \text{ mL}$, and $T = 298.15 \text{ K}$).

3.2.6 Selectivity study. Selective adsorption of the binary mixtures of U(VI)/Cu(II), U(VI)/Zn(II), U(VI)/Mg(II), U(VI)/La(III) and U(VI)/Ce(III) was investigated to evaluate the selectivity of IIP in a batch mode. The selectivity parameters such as distribution coefficient (K) and selectivity coefficient ($S_{U/M}$) were shown in Table 5. The obtained result revealed that the IIP were able to selectively adsorb U(VI) in the presence of competitive ions, which could be attributed to the creation of the specific recognition sites for U(VI) and the dense polymer layer coated on the material surface in the imprinting process.

Table 5 Selective sorption of U(VI) on IIP.

ions	$K (\text{mL g}^{-1})$	$S_{U/M}$
U(VI)/Cu(II)	253400/132	1920
U(VI)/Zn(II)	622000/9.8	6.32×10^4
U(VI)/Mg(II)	488500/5.7	8.63×10^4
U(VI)/La(III)	224400/40.8	5490
U(VI)/Ce(III)	24050/33.8	711

3.2.7 Reusability study. In order to test the reusability of IIP, adsorption-desorption cycles were repeated five times using 1 M HCl solution as the eluent and the result was shown in Fig. 5. It can be obviously seen from Fig. 6 that the prepared IIP can be efficiently regenerated and reused without a significant decrease in the percent uptake of U(VI) even after 5 cycles. The results indicated that IIP has excellent reusability and stability.

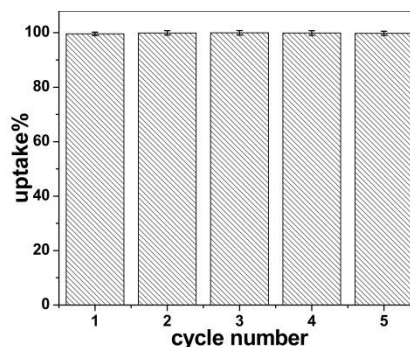


Fig. 6 Reusability of IIP towards U(VI) ($C_0 = 5 \text{ mg L}^{-1}$, $t = 3 \text{ h}$, $\text{pH} = 5.0$, $W = 60 \text{ mg}$, $V = 10 \text{ mL}$, and $T = 298.15 \text{ K}$).

4. Conclusions

A novel, facile and efficient route was developed to prepare highly selective U(VI)-imprinted polymer. The peroxide and hydroperoxide introduced by pre-irradiation in air could be effectively decomposed to initiate graft polymerization at a relatively low temperature in the presence of U(VI). The sorption of U(VI) on the IIP from the aqueous solution was evaluated by batch experiments. The results suggested that the adsorption process is pH dependent and the adsorption kinetics followed the pseudo-second order kinetic model. Also,

the Langmuir adsorption isotherm was fitted better with the experimental data and the calculated maximum adsorption capacity was 46.42 mg g⁻¹. Moreover, the U(VI)-imprinted polymer exhibited excellent adsorption selectivity and affinity toward U(VI). Meanwhile, IIP has good reusability and stability. Hence, the synthesized U(VI)-imprinted polymer is an excellent adsorbent for the selective separation and preconcentration of U(VI). This work may provide a new approach to prepare novel adsorbents for highly efficient removal of uranium(VI) from aqueous solution.

Acknowledgements

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