

Adsorptive features of polyacrylic acid hydrogel for UO_2^{2+}

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Abstract Polyacrylic acid hydrogel was synthesized by Free Radical polymerization and characterized by means of FTIR. The FTIR results show that the carboxylic groups in the complexes coordinated to the metal ions in the form of two dentate. The effects of contact time, solid/liquid ratio, pH value, and initial concentration on the adsorption of UO_2^{2+} ions onto polyacrylic acid were investigated. The adsorption of UO_2^{2+} ions was highly dependent on the initial pH of metal ions solution and initial metal ions concentration. The adsorption kinetic data indicated that the chemical adsorption was the swiftness processes, the adsorption equilibrium could be achieved within 15 min. And there are very good correlation coefficients of linearized equations for Freundlich model, which indicated that the sorption isotherm of the hydrogel for UO_2^{2+} can be fitted to the Freundlich model. It was found that the maximum adsorption quantity of UO_2^{2+} was 1,179 mg/g. After five times of repeated tests for the hydrogel it still remained its excellent adsorption.

Keywords Polyacrylic acid · Hydrogel · Adsorption · Uranium(VI)

Introduction

Uranium is widely spread element throughout the environment. The main sources of uranium are soils, tailings of some minerals processing activities, black sand and sea water, and so on [1]. Uranium has different applications including nuclear power plants, manufacture of nuclear weapons, the electron microscope and glass and pottery glaze [2]. Excessive amounts of uranium have entered into environment through the activities of nuclear industry by applications [3]. Uranium disposed into the environment can eventually reach the top of the food chain and be ingested by humans, causing harmful diseases such as lung, pancreatic and liver and even death [4, 5]. Therefore, methods for the removal of Uranium from polluted and waste water are of great importance.

Various techniques are employed for the removal of uranium ions from waste waters and radioactive wastes. Which are chemical precipitation [6], ion exchange [7], solvent extraction [8], membrane processes [9], chromatographic extraction [10], flotation and adsorption [11, 12]. Most of these methods suffer from technical, economic and health problems related to selectivity, long time of extraction and large quantity of hazardous materials used. However, with recent developments in resin technology, a great deal of attention has been paid to polymer materials such as hydrogel [13, 14], which have suitable functional groups (such as carboxylate) containing O, N, as well as S and P as donor atoms capable of interaction with metal ions [15].

Hydrogel is a three-dimensional network of hydrophilic polymers crosslinked by chemical or physical interactions [16, 17], and can be prepared with different functional groups such as carboxylic acid, amine, hydroxyl, and sulfonic acid groups. These groups attached onto the polymeric networks can be tailored easily for a specific application [18]. It has

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inherently hydrophilic network, but not dissolve in aqueous solution. Owing to higher adsorption rate and adsorption capacity, polymer hydrogels can provide many advantages as a novel type, fast-responsive, and high-capacity adsorbent materials for the removal of metal ions from aqueous solution [19–22]. Furthermore, hydrogels can be synthesized in bead form via inverse suspension crosslinking [23]. Owing to its chemical stabilities, good mechanical strength, the relatively large surface area and uniform particle size and shape [24, 25], hydrogel are the most promising materials which can be used to remove metal ions.

In this work, cross-linked PAA polymeric hydrogel was synthesized by the reaction of radical polymerization, which can not be dissolved in the aqueous solution and organic solvents. Due to the presence of a large amount of functional carboxylic groups, this adsorbent is expected to show higher affinity to metal ions via the chelating interaction between the carboxylic groups and UO_2^{2+} . The influence of experimental conditions such as pH value and initial UO_2^{2+} concentration were studied. The Freundlich equations were used to fit the equilibrium isotherm. The attached UO_2^{2+} can be desorbed from this adsorbent by a small amount of inorganic acid. This information will be useful for further applications of system design in the treatment of practical radioactivity waste effluents.

Experimental

Materials

AA (96 %, Chemical reagent, Tianjin) was distilled under reduced pressure before polymerization, ammonium persulfate (APS, initiator) was obtained from Aldrich Chemical Co., Inc. *N,N*-methylene-bis-acrylamide (MBA, cross-linker) was purchased from Sigma-Aldrich Co., Ltd. Other chemicals were of analytical reagent grade used without further purification. The pH of the working solutions was adjusted to the desired value by the addition of 0.1 M HCl or 0.1 M NaOH solutions. All aqueous solutions were prepared by deionized water.

Methods

FTIR spectra of unloaded and loaded hydrogel were recorded on a Nicolet Avatar 360 FT-IR instrument using KBr discs in the 400–4,000 cm^{-1} region. Concentration of U(VI) was analyzed with the Arsenazo-III spectro photometric method [26] on a UV-722S spectrophotometer.

Synthesis of PAA

PAA was synthesized by radical polymerization with APS as an initiator. The monomers of AA and MBA were

solved in water at 50 °C under agitation. APS was added to this solution and the solution was heated at 75 °C for 5 h in a nitrogen atmosphere. The product were washed with deionized water until the unreacted substance and fluid wax were completely removed, the hydrogel was dried in vacuum chamber at room temperature for 2 days.

Determination of UO_2^{2+} in solution

Concentration of UO_2^{2+} was analyzed with the Arsenazo-III spectro photometric method on a Shimadzu UV-722S spectrophotometer. 1 mL UO_2^{2+} solution sample, 1 mL 0.5 M HCl and 1.0 mL 0.1 % Arsenazo-III aqueous solution were added to a 25 mL glass flask, respectively, the final solution volume was filled up to 25 mL by adding deionized water. After 15 min, the absorbance of the mixture liquid was measured at 650 nm. The calibration curve equation for UO_2^{2+} detection was absorbance = $0.4991C - 0.0126$ ($R^2 = 0.9994$), where C was the concentration of UO_2^{2+} . Measurements were made in double for each experiment with errors less than 5 %.

Adsorption experiments

The effect of pH on adsorption was studied by batch adsorption process varying the initial pH of solution from 0.5 to 9.0. Experiments were carried out by mixing approximately 30 mg of hydrogel with 5 mL of aqueous solution containing UO_2Cl_2 aqueous solution with the desired concentration and appropriate pH and shaking for 5 h in a thermostatic shaker bath at 25 °C. The mixture solution was centrifuged at 4,000 rpm for 10 min at room temperature and the metal-ion UO_2^{2+} concentration in the solution was determined by UV-Vis spectrophotometer at 650 nm as described above [27]. The amount of adsorption at equilibrium time t , q_e (mg/g), was calculated by:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where C_0 and C_e are the liquid-phase concentrations of UO_2^{2+} at initial and equilibrium time, respectively; V the volume of the solution (L); W is the mass of dry adsorbent used (g).

The adsorption removal efficiency of U(VI) from aqueous solution was calculated as follows:

$$\text{removal efficiency (\%)} R_m = (C_0 - C_f)/C_0 \times 100 \quad (2)$$

where C_f is the final metal-ion concentration.

Adsorption isotherm experiments were performed with solutions of different initial metal ions concentrations. The range of concentration of metal-ion solution prepared from stock solution was varied at pH 5.0. The adsorption experiments were repeated three times and the mean values are reported.

The ion selectivity of PAA hydrogels from solutions containing possible combinations of studied ions (Ca^{2+} , Mg^{2+} , UO_2^{2+}) at equivalent concentrations ($5 \times 10^{-3} \text{ mol/L}^{-1}$) was studied. Accurate amount of PAA hydrogels (30 mg) was shaking for 5 h in a thermostatic shaker bath at 25°C with a solution of the mixture. Then the mixture solution was centrifuged at 4,000 rpm for 10 min at room temperature and the metal-ion UO_2^{2+} concentration in the solution was determined by UV–Vis spectrophotometer at 650 nm.

In order to determine the potential reusability of the hydrogels, consecutive sorption–desorption cycles were repeated five times using the sorbent prepared following the procedure described in adsorption experiments. Desorption was done with 0.1 M HCl (UO_2^{2+}) (mass of loaded sorbent 30 mg; volume of solution 50 mL, duration of process 24 h). The sorption/desorption cycles were repeated for five times using 30 mg of the sorbent.

Results and discussion

Infrared spectra analysis

Figure 1 shows the FTIR spectra of PAA and PAA complexes. The FTIR spectra of the PAA complexes are different from that of the PAA hydrogel obviously. The sharp bands at $1,719(\text{V}_{\text{C=O}})$ and $1,459 \text{ cm}^{-1} (\text{V}_{\text{C-O}})$ show the presence of $-\text{COOH}$ group from PAA [28]. While in the complex of UO_2^{2+} two strong absorption bands lying at $1,530$ and $1,457 \text{ cm}^{-1}$ are observed, which are attributed to

the symmetric $\text{v}_s(\text{COO}^-)$ and asymmetric $\text{v}_{as}(\text{COO}^-)$ of carboxylate, respectively. Kakihana and Nagumo [29] showed that the nature of carboxylate coordination to a metal is conveniently obtained from a comparison of $\Delta\text{Vas-s}$. The determined $\Delta\text{Vas-s}$ for the two complexes show a bidentate chelate [29–31]. The absorptions at $3,438$ and $1,631 \text{ cm}^{-1}$ was attributed to O–H stretching and H–O–H bending vibrations of lattice water molecules in the PAA complexes [32]. The appearance of a peak at 919 cm^{-1} UO_2^{2+} loaded PAA is characteristic of $\text{O}=\text{U}=\text{O}$ stretching vibration [33]. The weak bands at ca 523 and 530 cm^{-1} are assigned to $\text{V}(\text{M}-\text{O})$ [34].

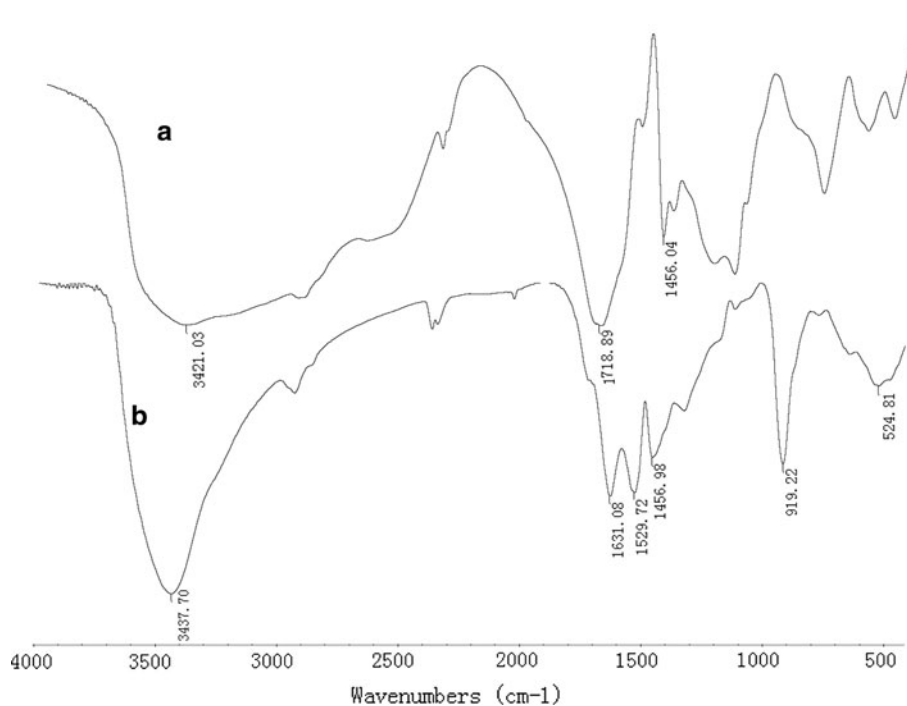
According to the results of composition determination, the structural unit of M-PAA was shown in Fig. 2, in which each UO_2^{2+} is bonded to two carboxylates in the chain of the polymer (not necessarily in only one chain), forming stable and repeatable building blocks.

Results of adsorption experiments

Dependence of pH values

The pH of the adsorptive medium is one of the most important parameter controlling the uptake of metal ions from solutions and it affect the surface charge of the adsorbent, degree of the ionization and speciation of the adsorbate [35, 36]. In this study, the adsorption experiments were conducted in the initial pH range of 1.0–8.0. As shown in Fig. 3, the effect of the pH values on the adsorption ratio (R_m) was important. The adsorption ratio (R_m) increases with the

Fig. 1 FTIR spectra of **a** PAA, **b** PAA complexes



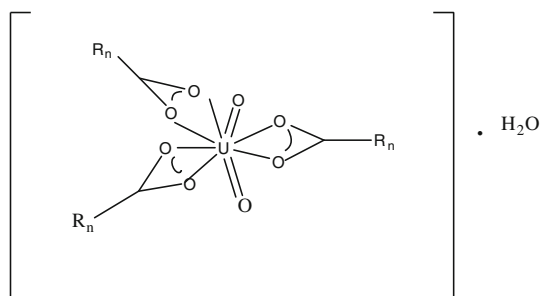


Fig. 2 The suggested structure of the complexes

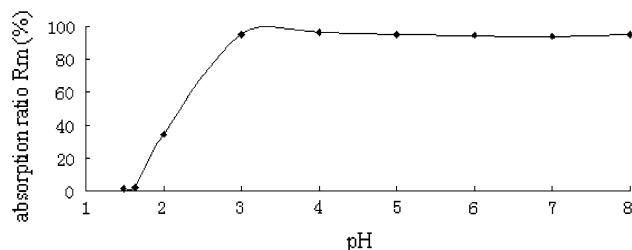
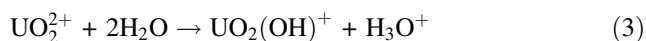


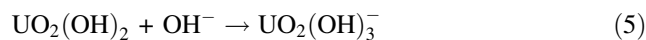
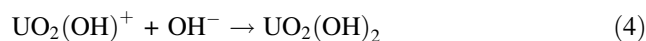
Fig. 3 Effect of pH on the adsorption of UO_2^{2+} onto PAA hydrogel
adsorption condition: initial concentration of metal ions $\text{UO}_2^{2+} = 4.255 \times 10^{-4}$ mol/L, room temperature, 5 h

increase of the solution pH values for the PAA hydrogels when pH below 3.0 for UO_2^{2+} R_m was not change with the increasing pH when the pH above 3.0 in the stronger acidic region, some $-\text{COO}-$ groups are transformed to $-\text{COOH}$ groups, leading the electrostatic attraction between adsorbent and adsorbate to diminish, and accordingly, the adsorption capacity decreases. With increasing the pH from 2 to 7, deprotonation is occurred and resulting in ionization of more carboxylic groups ($-\text{COOH}$) that can be transferred to the carboxylate ions (COO^-) participated in the hydrogel matrix [37]. The carboxyl ions have the stronger electrostatic attraction to the metal ions adsorbed than the carboxyl groups [38]. As a result, the adsorption capacity of metal ions increases rapidly.

The hydrolysis of UO_2^{2+} plays a significant role in determining the equilibrium between the UO_2^{2+} in solution and on adsorbent. As pH increases, UO_2^{2+} undergo a series of hydrolytic reactions and form species such as UO_2^{2+} , $\text{UO}_2(\text{OH})^+$, $\text{UO}_2(\text{OH})_2$ and $\text{UO}_2(\text{OH})_3^-[\text{Cl}]$. But in weakly acidic solution, the dominant species is $\text{UO}_2(\text{OH})^+$ which is formed as a hydrolytic product of UO_2^{2+} ions as:



So when the pH value of the aqueous phase was in the range 4.0–6.0, $\text{UO}_2(\text{OH})^+$ was strongly complexed with PAA and form a 1:2 complex. At higher pH values > 6.0, $\text{UO}_2(\text{OH})^+$ ions reacted with OH^- ions further and gradually formed a colloidal precipitate of $\text{UO}_2(\text{OH})_2$ and $\text{UO}_2(\text{OH})_3^-$ according to:



So at the highest pH value uranium should begin to precipitate as $\text{UO}_2(\text{OH})_2$ or $\text{UO}_2(\text{OH})_3^-$. At the highest pH value the solubility product of $\text{UO}_2(\text{OH})_2$ exceeded, therefore, UO_2^{2+} is removed from the solution by precipitation is not by adsorption. So in our experiment we choose pH 5.0 for U(VI) other parts experiment. Nevertheless, the PAA hydrogel can still be considered as an excellent candidate for removing UO_2^{2+} due to its wide pH application range.

Effect of initial concentration

The effect of the initial metal ions concentration on the adsorption removal efficiency was studied by contacting a fixed mass of PAA (30 mg) at a fixed temperature (25 °C) and initial pH 5.0 using a series of freshly prepared metal ion solutions. The results are shown in Fig. 4. The amount of metal ions adsorbed increases with an increasing concentration. As expected the adsorption capacity increased with the initial metal concentration. With more UO_2^{2+} present in solution, larger fraction of the active sites is involved in the adsorption process. At higher UO_2^{2+} concentrations adsorption capacity reached a plateau indicating saturation of the available binding sites on the adsorbent [39]. The steep slope at initial UO_2^{2+} concentrations is a desirable feature of the sorption system and the results indicates that a PAA bead is an efficient adsorbent for UO_2^{2+} . The maximum amount of metal ions adsorbed exceeds to 1,179 mg/g for UO_2^{2+} . As shown in Fig. 4 the ratio of adsorption decreases with increasing concentration, it can be seen that the adsorption capacity of PAA for UO_2^{2+} is rather high.

Adsorption kinetics

Agitation period is an important parameter which reflects the adsorption kinetics of an adsorbent at a given initial

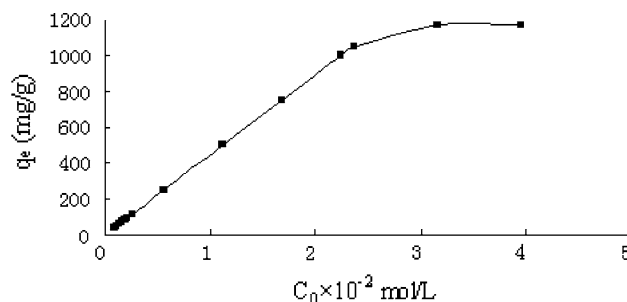


Fig. 4 Effect of the initial concentration on the adsorption behavior of UO_2^{2+} on PAA hydrogel

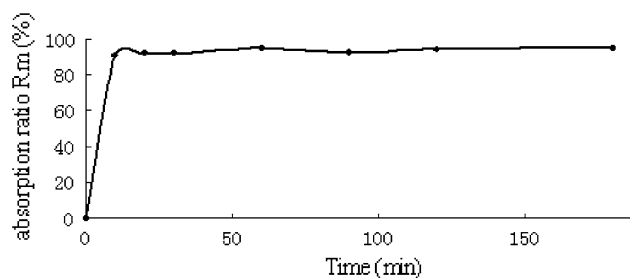


Fig. 5 Effect of agitation period on the adsorption of UO_2^{2+} on PAA hydrogel

adsorbate concentration. The effects of contact time on the adsorption capacity were investigated at an initial UO_2^{2+} concentration of 4.255×10^{-4} mol/L, as shown in Fig. 5. The adsorption of UO_2^{2+} onto PAA as a function of contact time illustrated that the adsorption rate was rapid and the adsorption equilibrium could be achieved within 15 min. This is because that the as-prepared adsorbent is consisted of flexible polymeric chains with super-hydrophilic characteristics [40]. When it is immersed in an aqueous solution, water molecules penetrate quickly into the hydrogel, resulting in a dimensional increase of polymeric networks. Then, the concentration gradient of UO_2^{2+} is formed at gel–water interface, and the diffusion of UO_2^{2+} into the gel is started. Due to the presence of a large amount of negatively charged $-\text{COO}^-$ groups, UO_2^{2+} moved from the external solution into the hydrogel can be adsorbed and trapped within the polymeric network, leading the adsorption system to reach equilibrium within a few minutes.

Adsorption isotherm

The adsorption isotherm is the most important information, which indicates how the adsorbent molecules distribute between the liquid and the solid phase when the adsorption process reaches an equilibrium state [41]. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms. In this study, The equilibrium data for U(VI) adsorption at 20 °C were modeled

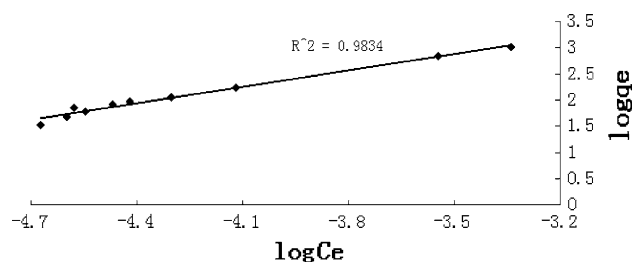


Fig. 6 Comparison of model fit of the Freundlich model to the experimental data for the adsorption of UO_2^{2+} onto PAA. Adsorbent dose 6 g/L, temperature 25 °C, pH 5.0, equilibrium time 5 h

Freundlich isotherm models. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. K is the Freundlich constant related to adsorption capacity and n is a constant indicative of intensity of adsorption. The Freundlich equation was used in the linearized form [42]:

$$\lg q_e = \lg K + 1/n \lg C_e \quad (6)$$

where K and n are Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. K and n can be determined from a linear plot of $\lg q_e$ against $\lg C_e$. The value of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity. It becomes more heterogeneous as its value gets closer to zero and a value of $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of cooperative adsorption [43, 44].

Figure 6 show that the adsorption of UO_2^{2+} on the cross-linked PAA hydrogel correlated well with the Freundlich equation under the concentration range studied. The numerical values of $1/n$ calculated as 1.0043 from respect slopes are above one, indicative of cooperative adsorption. These results are attributed to the hydrophilic nature of COO^- units in the PAA, which has a particular affinity to the transition metal ions, and the long polymer chain leading to an open porous structure that allows easy diffusion of metal ions to the chelating sites [45].

Ion selectivity and reusability of the hydrogel

The ability to selectively remove some particular metal ions from aqueous solution under competitive conditions is important in applications. Ion selectivity of the adsorbent in the presence of the studied ions with all possible combinations at equivalent concentrations (4.255×10^{-4} mol/L) was compared in Table 1. It can be seen that the hydrogel had the higher affinity UO_2^{2+} in the presence of both Ca^{2+} and Mg^{2+} at pH 5.0. The results indicated that the UO_2^{2+} removal efficiency was not affected by the others metal ions. So we can conclude that PAA can be effectively used for removing UO_2^{2+} from waste water. Further studies are required on value metal mixtures and on

Table 1 Ion selectivity of PAA hydrogel from solutions containing possible combinations of studied ions at equivalent concentrations (4.255×10^{-4} mol/L)

Ion combinations	Adsorption of UO_2^{2+} (%)
UO_2^{2+}	92.06
UO_2^{2+} , Ca^{2+}	92.65
UO_2^{2+} , Mg^{2+}	93.37
UO_2^{2+} , Ca^{2+} , Mg^{2+}	94.4

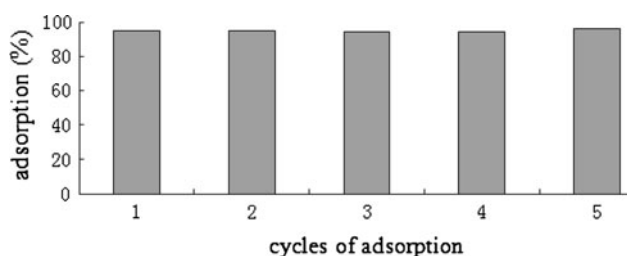


Fig. 7 The amount adsorbed for UO_2^{2+} as a function of adsorption–desorption cycle

industrial liquors which often contain a wide range of metal ions.

Desorption studies can help elucidating the mechanism of an adsorption process. If the UO_2^{2+} adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of UO_2^{2+} onto the adsorbent is by weak bonds. If the strong acid, such as HCl or HNO_3 can desorb the UO_2^{2+} , it can be said that the attachment of UO_2^{2+} onto the adsorbent is by ion exchange or electrostatic attraction [46]. In this study, the desorption of adsorbed UO_2^{2+} onto the as-prepared hydrogel was studied using 0.1 M HCl, as shown in Fig. 7. It is clear that the strong acid ($\text{pH} \leq 2$) can give the higher recovery of UO_2^{2+} , suggesting that the adsorption of UO_2^{2+} onto this hydrogel is mainly controlled by electrostatic attraction and chelated attraction [40].

An adsorbent, in addition to its good adsorption and desorption characteristics, must also exhibit a good regeneration ability for multiple uses. The Fig. 7 indicated that the hydrogel could easily be regenerated by 0.1 M HCl. No significant loss of the capacity during five cycles of adsorption–desorption. At this point, to the possibility of reusing the chelated hydrogel several times. This character of the possibility for reusing the hydrogel several times makes it economically suitable for use.

Conclusion

Polyacrylic acid hydrogel was synthesized by Free Radical polymerization characterized by means of FTIR. The FTIR results show that the carboxylic groups in the complexes coordinated to the metal ions in the form of two dentate. The polyacrylic acid hydrogel were found to have good adsorption capacity for UO_2^{2+} from aqueous solution. Batch adsorption experiments indicate that the adsorption equilibrium can be achieved within 10 min and the maximum amount of metal ions adsorbed exceeds to 1,179 mg/g for UO_2^{2+} at 25 °C and initial pH 5.0, meaning fast adsorption rate and high adsorption capacity of the as-prepared hydrogel for UO_2^{2+} . The as-prepared adsorbent can be applied in a wide pH range of 3–7. It was found that

the adsorption of UO_2^{2+} on the cross-linked PAA hydrogel correlated well with the Freundlich equation under the concentration range studied, UO_2^{2+} was desorbed successfully using 0.1 M HCl solution, and the adsorbent can be easily regenerated with no conspicuous losses in the adsorption capacity. The results presented here have confirmed the potential of polyacrylic acid hydrogel as an effective adsorbent for the removal of UO_2^{2+} from aqueous solutions.

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References

1. Prasada Rao T, Metilda P, Gladis JM (2006) Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination—an overview. *Talanta* 68:1047–1064
2. Eisenbud M, Gesell T (1997) Environmental radioactivity from natural, industrial, and military sources. Academic Press, Boston
3. Choppin GR, Morgenstern A (2000) Radionuclide separations in radioactive wastes disposal. *J Radioanal Nucl Chem* 243:45–51
4. Xie SB, Yang J, Chen C, Zhang XJ, Wang QL, Zhang C (2008) Study on biosorption kinetics and thermodynamics of uranium by *Citrobacter freundii*. *J Environ Radiact* 99:126–133
5. Van Horn JD, Huang H (2006) Uranium(VI) bio-coordination chemistry from biochemical, solution and protein structural data. *Coord Chem Rev* 250:765–775
6. Mellah AS, Chegrouche Barkat M (2007) The precipitation of ammonium uranyl carbonate (AUC): thermodynamic and kinetic investigations. *Hydrometallurgy* 85:163–171
7. Gu B, Ku Y, Brown GM (2005) Sorption and desorption of perchlorate and U(VI) by strong-base anion-exchange resins. *Environ Sci Technol* 39(3):901–907
8. Kanekar AS, Pathak PN, Mohapatra PK, Manchanda VK (2010) Comparative extraction efficiencies of tri-*n*-butyl phosphate and *N,N*-dihexyloctanamide for uranium recovery using supercritical CO_2 . *J Radioanal Nucl Chem* 283:789–796
9. Kuhu AT (1972) Electrochemistry of cleaner environments. Plenum Press, New York
10. Dietz ML, Philip HE, Sajdak LR, Chiarizia R (2001) An improved extraction chromatographic resin for the separation of uranium from acidic nitrate media. *Talanta* 54(6):1173–1184
11. Jung Y, Kim S, Park S, Kim JM (2008) Application of polymer-modified nanoporous silica to adsorbents of uranyl ions. *Colloids Surf A* 313–314:162–166
12. Tsuruta T (2011) Biosorption of uranium for environmental applications using bacteria isolated from the uranium deposits. In: *Microbes and Microbial Technology*, Chap 11, pp 267–281
13. Unuabonah EI, Adebowal KO, Olu-owolabi BI, Yang LZ, Kong LX (2008) Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: equilibrium and thermodynamic studies. *Hydrometallurgy* 93:1–9
14. Wang CC, Chang CY, Chen CY (2001) Study on metal ion adsorption of bifunctional chelating/ion-exchange resins. *Macromol Chem Phys* 202(6):882–890
15. Biswas M, Mukterjee A (1994) Synthesis and evaluation of metal-containing polymers. *Adv Polym Sci* 115:89–123

16. Wang Q, Mynar JL, Yoshida M, Lee E, Lee M, Okuro K, Kinbara K, Aida T (2010) High-water-content hydrogel by mixing clay and dendritic. *Mol Glue* 463:339–343
17. Özeroğlu C, Doğan E, Keçeli G (2011) Investigation of Cs(I) adsorption on densely crosslinked poly(sodium methacrylate) from aqueous solutions. *J Radioanal Nucl Chem* 289: 577–586
18. Wang Q, Xie X, Zhang X, Zhang J, Wang A (2010) Preparation and swelling properties of pH-sensitive composite hydrogel beads based on chitosan-g-poly (acrylic acid)/vermiculite and sodium alginate for diclofenac controlled release. *Int J Biol Macromol* 46:356–362
19. Paulino AT, Guilherme MR, Reis AV, Campese GM, Muniz EC, Nozaki J (2006) Removal of methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide. *J Colloid Interface Sci* 301:55–62
20. Yetimoğlu EK, Kahraman MV, Bayramoğlu G, Ercan O, Apohan NK (2009) Sulfathiazole-based novel UV-cured hydrogel sorbents for mercury removal from aqueous solutions. *Radiat Phys Chem* 78:1800–1806
21. Zheng Y, Zhang J, Wang A (2009) Fast removal of ammonium nitrogen from aqueous solution using chitosan-g-poly(acrylic acid)/attapulgit composite. *Chem Eng J* 155:215–222
22. Liu Y, Zheng Y, Wang A (2010) Enhanced adsorption of methylene blue from aqueous solution by chitosan-g-poly (acrylic acid)/vermiculite hydrogel composites. *J Environ Sci* 22:486–493
23. O'Connor SM, Gehrke SH (1997) Synthesis and characterization of thermally-responsive hydroxypropyl methylcellulose gel spheres. *J Appl Polym Sci* 66:1279–1290
24. Li N, Bai RB (2005) A novel amine-shielded surface cross-linking of chitosan hydrogel beads for enhanced metal adsorption performance. *Ind Eng Chem Res* 44:6692–6700
25. Yan WL, Bai RB (2005) Adsorption of lead and humic acid on chitosan hydrogel beads. *Water Res* 39:688–698
26. Wei M, Liao JL, Liu N, Zhang D, Kang HJ, Yang YY, Yong Y, Jin JN (2007) Interaction between uranium and humic acid (I): adsorption behaviors of U(VI) in soil humic acids. *Nucl Sci Tech* 18:287–293
27. Wang GH, Liu JS, Wang XG, Xie ZY, Deng NS (2009) Adsorption of uranium(VI) from aqueous solution onto cross-linked chitosan. *J Hazard Mater* 168:1053–1058
28. Liu TH, Fang J, Zhang Y, Zeng ZZ (2008) The effect of salt and pH on the phase transition behaviors of pH and temperature-responsive poly(*N,N*-dimethylacrylamide-co-methylacrylic acid). *Macromol Res* 16(8):670–675
29. Kakihana M, Nagumo T (1987) Coordination structures for uranyl carboxylate complexes in aqueous solution studied by IR and carbon-13 NMR spectra. *J Phys Chem* 91:6128–6136
30. Liu TH, Duan GH, Zeng ZZ (2009) Synthesis and characterization of cerium, thorium, and uranyl complexes with (E)-4-(4-methoxyphenoxy)-4-oxobut-2-enoic acid. *J Coord Chem* 62(13): 2203–2211
31. Nakamoto K (1986) Infrared spectra and raman spectra of inorganic and coordination compounds. Wiley, New York
32. Kuppusamy K, Sivasankar BN, Govindarajan S (1996) Preparation and thermal reactivity of hydrazinium uranyl carboxylates. *Thermochim Acta* 274:139–148
33. Rivas BL, Maturana HA, Ocampo X, Peric IM (1995) Adsorption behavior of Cu^{2+} and UO_2^{2+} ions on crosslinked poly[2,2-bis(acrylamido)acetic acid]. *J Appl Polym Sci* 58:2201–2205
34. Yang ZY, Yang RD, Li FS, Yu KB (2000) Crystal structure and antitumor activity of some rare earth metal complexes with Schiff base. *Polyhedron* 19:2599–2604
35. Riaz Q (2012) A study of the factors affecting the adsorption of cobalt ions onto Pakistani coal powder from solutions. *J Radioanal Nucl Chem*. doi:10.1007/s10967-012-2189-9
36. Lu S, Guo Z, Zhang C, Zhang S (2011) Sorption of Th(IV) on MX-80 bentonite: effect of pH and modeling. *J Radioanal Nucl Chem* 287:621–628
37. Ma JH, Xu YJ, Fan B, Liang BR (2007) Preparation and characterization of sodium carboxymethylcellulose/poly(*N*-isopropylacrylamide)/clay semi-IPN nanocomposite hydrogels. *Eur Polym J* 43(6):2221–2228
38. Zhao L, Mitomo H (2008) Adsorption of heavy metal ions from aqueous solution onto chitosan entrapped CM-cellulose hydrogels synthesized by irradiation. *J Appl Polym Sci* 110:1388–1395
39. Duan GJ, Liu TH, Wu WS, Yang Y (2012) Adsorption of UO_2^{2+} from aqueous solution onto copolymers of styrene and maleic anhydride. *J Radioanal Nucl Chem*. doi:10.1007/s10967-012-2275-z
40. Zheng Y, Liu Y, Wang A (2011) Fast removal of ammonium ion using a hydrogel optimized with response surface methodology. *Chem Eng J* 171:1201–1208
41. Ansari SA, Mohapatra PK, Manchanda VK (2007) Synthesis of *N,N'*-dimethyl-*N,N'*-dibutyl malonamide functionalized polymer and its sorption affinities towards U(VI) and Th(IV) ions. *Talanta* 73:878–885
42. Pang C, Liu YH, Cao XH, Li M, Huang GL, Hua R, Wang CX, Liu YT, An XF (2011) Biosorption of uranium(VI) from aqueous solution by dead fungal biomass of *Penicillium citrinum*. *Chem Eng J* 170:1–6
43. Fytianos K, Voudrias E, Kokkalis E (2000) Sorption-desorption behavior of 2,4-dichlorophenol by marine sediments. *Chemosphere* 40:3–6
44. Rauf MA, Bukallah SB, Hamour FA, Nasir AS (2008) Adsorption of dyes from aqueous solutions onto sand and their kinetics behavior. *Chem Eng J* 137:238–243
45. Kay GM, Blair HS, Gardner JR (1982) Adsorption of dyes on chitin. I. Equilibrium studies. *J Appl Polym Sci* 27:3043–3057
46. Mall ID, Srivastava VC, Kumar GVA, Mishra IM (2006) Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. *Colloids Surf A* 278:175–187