

Studies on the recovery of uranium from nuclear industrial effluent using nanoporous silica adsorbent

H. Sepehrian · M. Samadfam · Z. Asadi

Received: 27 February 2011 / Revised: 12 July 2011 / Accepted: 19 November 2011 / Published online: 20 April 2012
© CEERS, IAU 2012

Abstract In this paper, the sorption of uranium onto nanoporous silica adsorbent in the presence of nitrate, sulfate, chloride, fluoride and phosphate was studied. The effect of contact time between the nanoporous sorbent and aqueous solution, pH and initial concentration of uranium was also investigated. Uranium sorption onto nanoporous silica adsorbent is a very fast process as sorption rate increases with pH increment. Optimum pH for uranium sorption was 4–8. Experimental sorption isotherm is successfully described by Langmuir and Freundlich models. The results obtained by batch experiments showed that the presence of high concentration of nitrate, sulfate, chloride and phosphate anions alone had no interference with uranium recovery. However, the presence of fluoride ions (>250 mg/L) decreases uranium sorption by about 55 %. The results also showed that the presence of phosphate ions (about 300 mg/L) in solution could remove fluoride interference completely. Finally, the efficiency of the nanoporous silica adsorbent for uranium recovery from wastewater of the uranium conversion facility was investigated.

Keywords Anions interference · Langmuir and Freundlich models · Uranium adsorption

Introduction

The recovery of nuclear elements such as uranium from aqueous systems, especially from industrial effluents has recently become the centre of a wide interest in exploiting undeveloped energy sources and environmental control (Nakajima and Sakaguchi 1999). Recovery of uranium was reported over years by various methods like liquid–liquid extraction (LLE), ion exchange, nano/ultra filtration, biosorption, coprecipitation, electrodeposition, solid phase extraction (SPE), imprinted polymers, liquid membranes, resin-in-pulp, solid state reaction, etc. (Michard et al. 1996; Tsuruta 2002; Kulkarni 2003; Chaudhury et al. 2003; Amamoto et al. 2005; Mirjalili and Roshani 2007; James et al. 2009; Akhtar et al. 2009; Singh et al. 2009).

In the industrial effluent, uranium is capable of forming anionic species mainly, uranyl carbonate, uranyl, fluoride, uranyl chloride, uranyl phosphate or uranyl sulfate. The strange base anion exchanger is the most suitable resin for uranium when it is mainly as anionic complexes. Anion exchange resins have been successfully employed to recover uranium in mining industry, especially from leach liquor (Zhang and Clifford 1994; Song et al. 1999; Huikuri and Salonen 2000; Chellam and Clifford 2002). The recovery of uranium from industrial effluents by resins and the influence of carbonate, fluoride and ammonium were studied on the uranium uptake and concluded that the uranium concentration in solution relative to other ions was the main

H. Sepehrian (✉)
Nuclear Science and Technology Research Institute,
AEOI, P.O. Box 11365/8486, Tehran, Iran
e-mail: hsepehrian@aeoi.org.ir

M. Samadfam · Z. Asadi
Department of Energy Engineering,
Sharif University of Technology,
Tehran, Iran

factor which interfered in the separation process (Nascimento et al. 2004; Ladeira and Morais 2005).

The discovery of nanoporous materials (Beck et al. 1992; Feng et al. 1997; Liu et al. 1998) with large surface area and uniform pores, wide opened a new approach for the removal/entrapment of persistent inorganic pollutants (Shin et al. 1999; Jal et al. 2004; Li et al. 2007; Mangrulkar et al. 2008; Benhamou et al. 2009; Idris et al. 2011). MCM-41 (Mobile Crystalline Material) is a nanoporous silicate featuring hexagonally packed arrays of one-dimensional cylindrical pores with a uniform pore distribution, large specific surface area and large pore volume (Beck et al. 1992).

In this paper, sorption behavior of uranium on nanoporous MCM-41 in the presence of some anions such as sulfate, fluoride, chloride, nitrate and phosphate was studied. The effect of contact time, pH, initial concentration and interference of anions was investigated. This research was carried out in the 2011 for uranium recovery from the uranium conversion facility (UCF, Esfahan), Iran.

Materials and methods

Reagents

All the chemicals used were of analytical grade from Merck, except cetyltrimethylammonium bromide (CTAB) which was supplied by Aldrich (UK).

Apparatus

A Philips X'pert powder diffractometer system with $\text{Cu-K}\alpha$ ($\lambda = 1.541 \text{ \AA}$) radiation was used for X-ray studies. XRD analysis was performed from 1.5° (2θ) to 10.0° (2θ) at a scan rate of 0.02° (2θ) s^{-1} . Nitrogen sorption studies were made with a Quantachrome NOVA 2200e instrument. Nitrogen sorption and desorption isotherms of the adsorbent were determined at 77 K and specific surface area was determined by applying the BET equation to the isotherm (Brunauer et al. 1938). The pore size distribution was calculated using the sorption branch of the isotherm and the Barrett–Joyner–Halenda (BJH) formula (Barrett et al. 1951). The scanning electron micrographic image was recorded using a Philips microscope. TEM image was taken by JEM1200 EX with 100 kV acceleration voltages. pH measurements were made with a Schott CG841 pH-meter (Germany). Quantitative determination of inorganic ions was made using an inductively coupled plasma-optical emission spectrometer (ICP-OES) of Varian Liberty 150-Axial.

Anions, such as F^- , Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} in waste water were determined by ion-chromatography of Metrohm model 733. A waterbath shaker model CH-4311 (Infors AG) was used in the determination of distribution coefficients.

Preparation of nanoporous silicate MCM-41

The nanoporous MCM-41 was prepared by mixing sodium silicate as silicon source, and CTAB as surfactant under non-thermal condition (Sepehrian et al. 2010). In a typical procedure, 0.6 g CTAB was dissolved in 23 g of demineralized water, then, 3 g of sodium silicate was added and it was stirred for 30 min. The pH value was adjusted at 9 by adding sulfuric acid (2 M). The stirring was continued for 4 h. A bulky white gelatinous precipitate was formed. The resulting gel was transferred to a Teflon vessel and was left for 24 h at room temperature. Then the product was filtered, washed thoroughly with demineralized water and then dried at 50°C for 12 h. Finally, for removing surfactant, this material was calcined at 540°C for 6 h.

Procedure for sorption studies

Sorption studies of the uranium ion on the MCM-41 adsorbents were carried out using batch method. In this procedure, 20 mg of adsorbent material was added to a 10 mL buffered solution of 2–125 mg/L uranium ions. The pH of the solution was adjusted with sodium hydroxide and hydrochloric acid. The suspension was stirred for a preselected period of time using a water shaker bath. Then it was filtered and the amount of uranium ion was determined by ICP. The sorption rate (%) and the sorption concentration (q , mol/g) were calculated using the relationships:

$$\text{Sorption rate (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

$$q \text{ (mol/g)} = (C_i - C_f) \times \frac{V}{m} \quad (2)$$

where m is mass of adsorbent, V the volume of uranium aqueous solution contacted with adsorbent (mL), C_i the initial concentration of uranium and C_f the equilibrium concentration of uranium (mg/L) after sorption.

Effect of anions

The effect of anions on the uranium sorption was investigated at a constant concentration of uranium. In batch

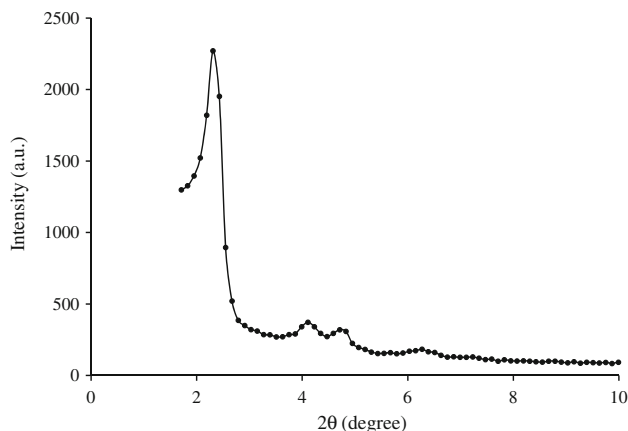


Fig. 1 XRD pattern of the nanoporous MCM-41

experiments, 20 mg of MCM-41 adsorbent was equilibrated with 10 mL of the solution containing 5 mg/L of uranium ions with various concentrations of the anions [sulfate (500–3,000 mg/L), fluoride (250–5,000 mg/L), chloride (50–2,500 mg/L), nitrate (10–10,000 mg/L) and phosphate (10–300 mg/L)]. For competition experiments of anions, the effect of fluoride ions on the uranium sorption was also studied in the presence of other anions.

Results and discussion

Characterization of adsorbent

XRD analysis

The XRD pattern of the calcined MCM-41 is presented in Fig. 1. The XRD pattern shows a strong diffraction at 2θ smaller than 3° along with the presence of small peaks that confirms the formation of nanoporous MCM-41 (Beck et al. 1992). This result is characteristic of hexagonal pore structure.

Nitrogen sorption-desorption studies

The nitrogen sorption-desorption isotherm and corresponding pore size distribution of the MCM-41 are given in Fig. 2. N_2 sorption-desorption isotherm showed a typical IV-type sorption profile consisting of a condensation due to the formation of nanopores (Fig. 2). Table 1 shows the specific surface area, pore volume and pore size of the nanoporous MCM-41.

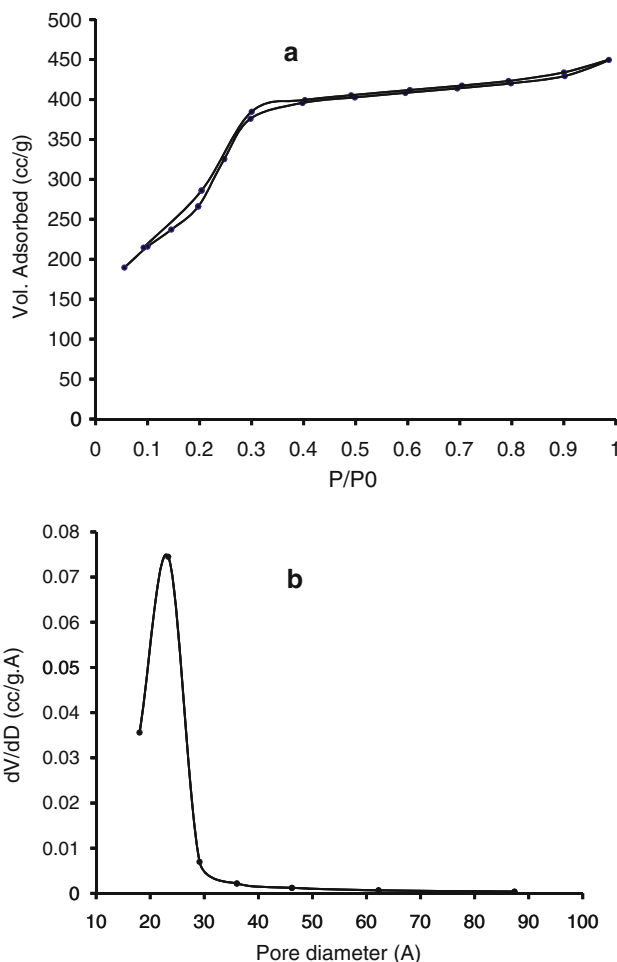


Fig. 2 a Nitrogen sorption-desorption isotherm and b pore size distribution of the nanoporous MCM-41

Table 1 Physical characteristics of the nanoporous MCM-41

Adsorbent	XRD d_{100} (Å)	Unit cell parameter ^b (a_0) (Å)	Pore volume (cc/g)	BET surface area (m ² /g)	pore diameter (Å)
MCM-41	31.9	36.8	0.89	1,395	21.3

^a Calculated from the equation $a_0 = 2d_{100}/\sqrt{3}$

Scanning electron micrograph

The SEM image of the nanoporous MCM-41 is given in Fig. 3. The SEM image exhibit uniform spherical crystallites.

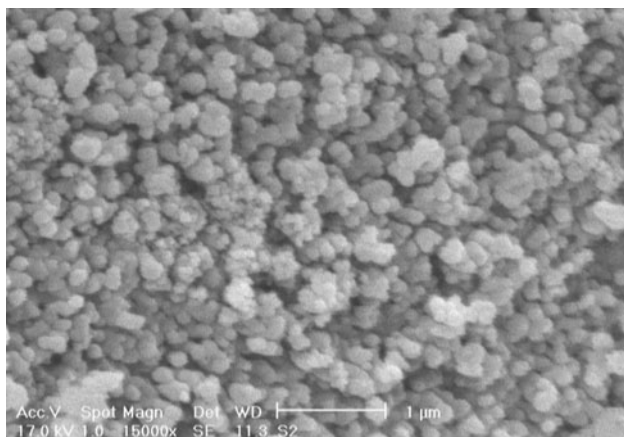


Fig. 3 Scanning electron micrograph of the nanoporous MCM-41

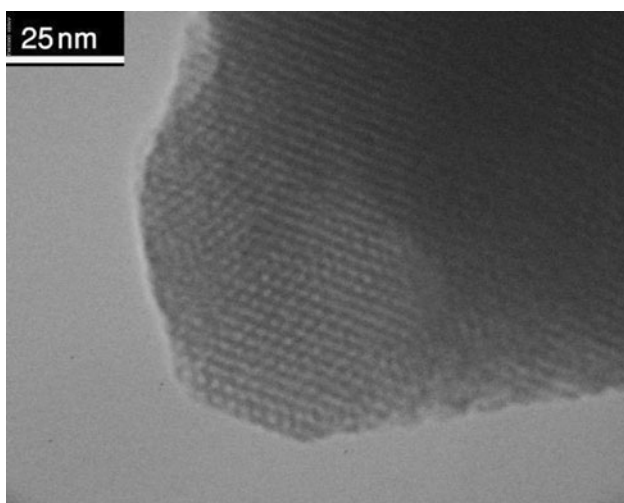


Fig. 4 Transmission electron micrograph of the nanoporous MCM-41

Transmission electron micrograph

The transmission electron micrograph of the nanoporous MCM-41 is given in Fig. 4. The TEM image shows that the pore diameter of the channels calculated from N_2 sorption measurement of the nanoporous MCM-41 is about 20 Å.

Adsorption studies

Table 2 shows chemical analysis of UCF waste water. On basis of this result next experiments have been designed.

Table 2 Results of chemical analysis of UCF waste water

Compound	Concentration (ppm)
U	3 ± 0.2
Si	53.4
Fe	1.4
Na	6,446
Ca	1.9
Cl^-	2,527
F^-	4,842
NO_3^-	9,920
SO_4^{2-}	2,654
PO_4^{3-}	248
pH	6.5

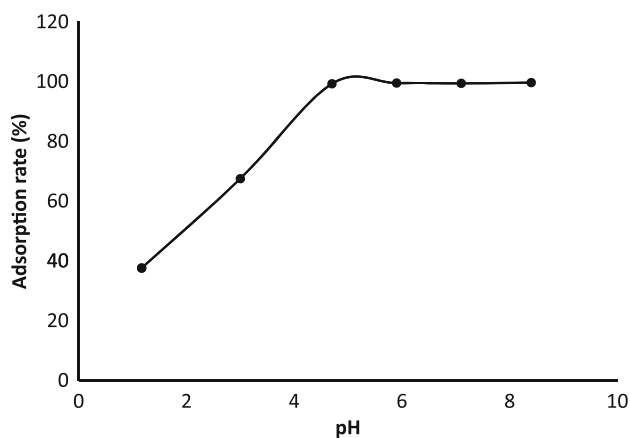


Fig. 5 Effect of pH on sorption of uranium onto the nanoporous MCM-41 (temperature = 25 °C, $C_0 = 5$ mg/L and contact time = 2 h)

Effect of pH

In general, the sorption of uranyl ions on oxides is viewed as an ion exchange reaction between the surface hydroxyl groups (Si–OH) and the uranyl ions (UO_2^{2+}) or its hydrolysis products (His and Langmuir 1985; Lieser et al. 1992; Schmeide et al. 2000). The sorption of uranium was studied in the pH range of 1–8.

As seen in Fig. 5, the sorption of uranium varied significantly with the pH of solution. When $pH \leq 2.0$, UO_2^{2+} as a main cation species existed in an acidic solution. In this acidic region, silanol groups onto pores of MCM-41 were as $SiOH_2^+$. So, in $pH \leq 2.0$, it was found that U(VI) showed no sorption towards MCM-41. After $pH \geq 2$ with an increase in basicity of the aqueous solution, $Si-OH_2^+$ as a cation gradually converted to a natural Si–OH by reacting



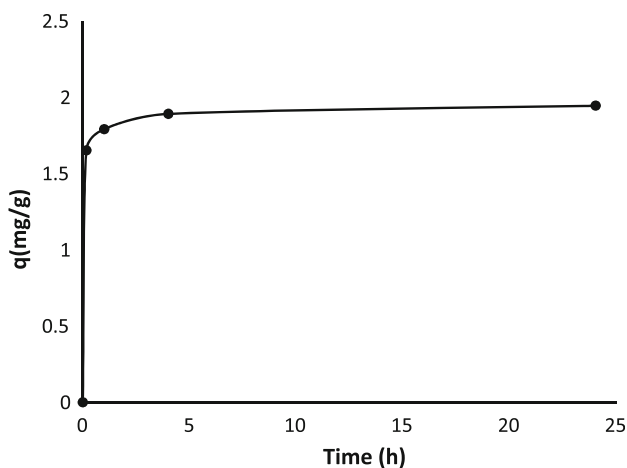


Fig. 6 Effect of contact time on sorption of uranium onto the nanoporous MCM-41 (temperature = 25 °C, pH = 6.5 and $C_0 = 5$ mg/L)

with OH^- , while UO_2^{2+} gradually hydrolyzed to $\text{UO}_2(\text{OH})^+$ by connecting with OH^- . Since $\text{UO}_2(\text{OH})^+$ was a complexible species with the neutral Si-OH, so, U(VI) showed sorption towards MCM-41 adsorbent with an increase in pH value. The next experiments in this study were carried out at natural pH (6.5).

Kinetic study

The sorption kinetics experiments were carried out at an initial uranium concentration of 5 mg/L at natural pH. As shown in Fig. 6 almost 90 % uranium is adsorbed after 10 min which is efficient time when comparing with other adsorbents (Hongxia and Zuyi 2002; Hongxia et al. 2005). The fast sorption rate suggests that the silanol groups are readily available and easily accessible probably because the uniform nanoporous channels of the MCM-41 adsorbent facilitate the uranium ions transportation in the process.

Sorption isotherms

The linear sorption isotherms are plotted in Fig. 7. Among various binding models, Langmuir and Freundlich isotherms have been frequently employed to describe experimental data of sorption isotherms. The Langmuir sorption isotherm is mathematically expressed as:

$$q_e = \frac{K_1(q_{\max})C_e}{1 + K_1C_e} \tag{3}$$

where q_e ($\mu\text{mol/g}$) is the amount of analyte bound to adsorbent, C_e (μM) the equilibrium concentration of adsorbate in solution, q_{\max} the maximum sorption

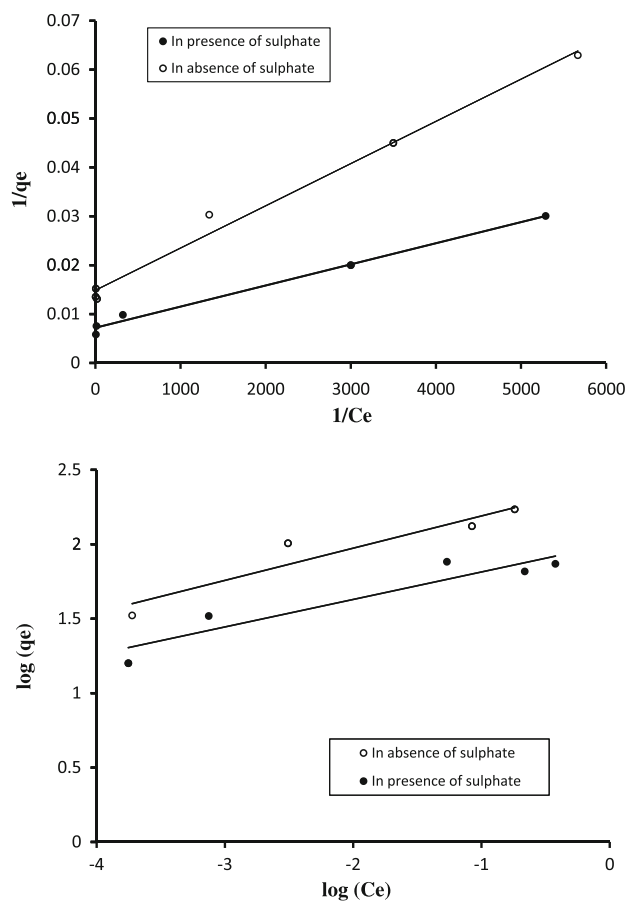


Fig. 7 Experimental sorption data (points) and Langmuir and Freundlich isotherms fit for the nanoporous MCM-41 (lines)

Table 3 Isotherm parameters obtained by using linear method

Condition	Fitting parameters					
	Langmuir			Freundlich		
	R^2	K_1 (L/ μmol)	q_{\max} (mg/g)	R^2	K_f ($\mu\text{mol/g/mM}$)	m
In the presence of sulfate	0.99	1,245.24	18.08	0.88	99.77	0.18
In the absence of sulfate	0.99	801.24	36.02	0.90	257.04	0.22

capacity ($\mu\text{mol/g}$) and K_1 the constant for a given adsorbate and adsorbent at a particular temperature. Langmuir equation is the most common model employed to describe the sorption process in homogenous systems. The equation constant values q_{\max} and K_1 are calculated from the experimental data (Table 3). For comparative purposes the experimental data have been fitted to the well-known Freundlich equation.

$$q_e = K_f C_e^m \tag{4}$$

K_f and m are constants for a given adsorbate and adsorbent at a particular temperature. From the values of R^2 summarized in Table 3, it may be calculated that both equations fit reasonably well with the experimental data, although the Langmuir equation provides a better fitting than the Freundlich one.

Effect of anions presence

Effects of nitrate (NO_3^-), chloride (Cl^-), fluoride (F^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) on uranium sorption onto the nanoporous MCM-41 were evaluated (Fig. 8). The results showed that the presence of high concentration of the nitrate, chloride, sulfate and phosphate anions had no interference for uranium sorption. But the percent of uranium sorption was decreased in the presence of fluoride by about 55 %.

This maybe due to uranium existing as $\text{UO}_2\text{F}_n^{(2-n)+}$ complexes (Kirishima et al. 2004) in the presence of fluoride ions and it has no strange interaction with silanol groups in pores of nanoporous MCM-41. The results of uranium sorption in binary mixture of anions also showed that the fluoride interference has been decreased in the presence of phosphate anions (Fig. 9). This maybe due to the fact that the affinity complexation of uranium with phosphate is more than the fluoride ions and in the presence of phosphate, uranium is more as $\text{UO}_2(\text{PO}_4)_3^{4-}$ complex and fluoride is as free ions (F). The $\text{UO}_2(\text{PO}_4)_3^{4-}$ complexes have strong interaction with silanol groups in the pores of nanoporous MCM-41. It shows that uranium can be adsorbed on the nanoporous MCM-41 in the presence of phosphate anions in UCF waste waters in the

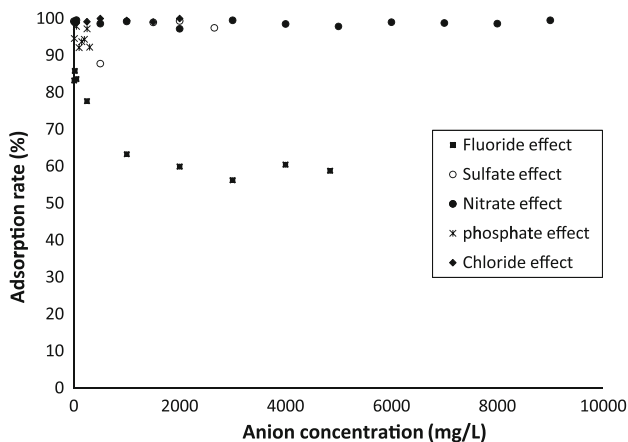


Fig. 8 Effect of anions concentration on uranium sorption [sulfate (500–3,000 mg/L), fluoride (250–5,000 mg/L), chloride (50–2,500 mg/L), nitrate (10–10,000 mg/L) and phosphate (10–300 mg/L)]

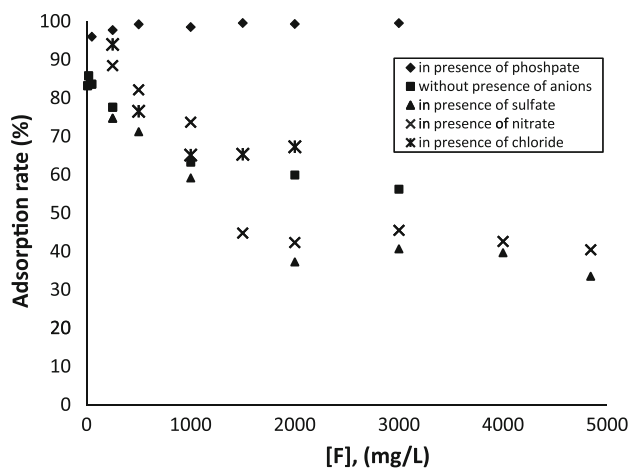


Fig. 9 Effect of fluoride in the presence of various concentration of other anions on uranium sorption [sulfate (3,000 mg/L), chloride (2,500 mg/L), nitrate (10,000 mg/L), phosphate (300 mg/L) and fluoride (250–5,000 mg/L)]

Table 4 Recovery data with various eluents

Eluents	Concentration (mol/L)	Recovery (%)
HCl	0.1	93
	0.5	73
	1.5	65
H ₂ SO ₄	0.1	72
	0.5	68
	2	58
HNO ₃	0.1	70
	0.5	70
	2	65

presence of other anions and/or adding phosphate anions to UCF waste waters can decrease interference of other anions.

Uranium recovery

Desorption behavior was also studied after washing the column with acid solution such as nitric acid, sulfuric acid and hydrochloric acid in various concentrations (Table 4). The results show that the highest recovery (93 %) was obtained with 0.1 mol/L HCl solution.

Conclusion

Nanoporous MCM-41 was used for uranium recovery and showed high capacity for uranium (36.02 mg/g in

the absence of anions and 18.08 mg/g in the presence of sulfate anion). The results obtained by batch experiments showed that the presence of high concentration of nitrate, sulfate, chloride and phosphate anions alone had no interference for uranium recovery. The result also shows that uranium can be adsorbed on the nanoporous MCM-41 in the presence of phosphate anions, in the presence of other anions and/or adding phosphate anions to waste waters can decrease the interference of other anions.

Acknowledgments The authors gratefully acknowledge the support of this work by analysis section, NFCRS, Nuclear Science and Technology Research Institute.

References

- Akhtar K, Khalid AM, Akhtar MW, Ghauri MA (2009) Removal and recovery of uranium from aqueous solutions by Ca-alginate immobilized *Trichoderma harzianum*. *Bioresour Technol* 100:4551–4558
- Amamoto I, Terai T, Oobayashi H, Fujit R (2005) Separation and recovery study of uranium from spent NaF (fillers). *J Phys Chem Solids* 66:602–607
- Barrett EP, Joyner LG, Halenda PP (1951) The determination of pore volume and area distributions in porous substances. I. computations from nitrogen isotherms. *J Am Chem Soc* 73:373–380
- Beck JS, Vartuli JC, Roth WJ, Leonowics ME, Kresge CT, Schmitt KD, Chu CTW, Olson DH, Sheppard EW, Mccullen SB, Higgins JB, Schlenker JL (1992) A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J Am Chem Soc* 114:10834–10843
- Benhamou A, Baudu M, Derriche Z, Basly JP (2009) Aqueous heavy metals removal on amine-functionalized Si-MCM-41 and Si-MCM-48. *J Hazard Mater* 171:1001–1008
- Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. *J Am Chem Soc* 60:309–319
- Chaudhury S, Singh Mudher KD, Venugopal V (2003) Recovery of uranium from fluoride matrix by solid state reaction routes. *J Nucl Mater* 322:119–125
- Chellam S, Clifford DA (2002) Physical–chemical treatment of groundwater contaminated by leachate from surface disposal of uranium tailings. *J Environ Eng* 128:942–952
- Feng X, Fryxell GE, Wang LQ, Kim AY, Liu J (1997) Functionalized monolayers on ordered mesoporous supports. *Science* 276:923–926
- His CKD, Langmuir D (1985) Adsorption of uranyl onto ferric oxyhydroxide: application of the surface site-binding model. *Geochim Cosmochim Acta* 49:1931–1941
- Hongxia Z, Zuyi T (2002) Sorption of uranyl ions on silica: effects of contact time, pH, ionic strength, concentration and phosphate. *J Radioanal Nucl Chem* 254:103–107
- Hongxia Z, Yongxin X, Zuyi T (2005) Sorption of uranyl ions on gibbsite: effects of contact time, pH, ionic strength, concentration and anion of electrolyte. *Colloid Surface Physicochem Eng Aspect* 252:1–5
- Huikuri P, Salonen L (2000) Removal of uranium from Finnish groundwaters in domestic use with a strong base anion resin. *J Radioanal Nucl Chem* 245:385–393
- Idris SA, Davidson CM, McManamon C, Morris MA, Anderson P, Gibson LT (2011) Large pore diameter MCM-41 and its application for lead removal from aqueous media. *J Hazard Mater* 185:898–904
- Jal PK, Patel S, Mishra BK (2004) Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta* 62:1005–1102
- James D, Venkateswaran G, Prasada Rao T (2009) Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material. *Micropor Mesopor Mater* 119:165–170
- Kirishima A, Kimura T, Tochiyama O, Yoshida Z (2004) Speciation study on complex formation of uranium(VI) with phosphate and fluoride at high temperatures and pressures by time-resolved laser-induced fluorescence spectroscopy. *Radiochim Acta* 92:889–896
- Kulkarni PS (2003) Recovery of uranium(VI) from acidic wastes using tri-*n*-octylphosphine oxide and sodium carbonate based liquid membranes. *Chem Eng J* 92:209–214
- Ladeira ACQ, Morais CA (2005) Effect of ammonium, carbonate and fluoride concentration on the uranium recovery by resins. *Radiochim Acta* 93:207–209
- Li J, Qi T, Wang L, Liu C, Zhang Y (2007) Synthesis and characterization of imidazole-functionalized SBA-15 as an adsorbent of hexavalent chromium. *Mater Lett* 61(2007):3197–3200
- Lieser KH, Quandt-Klenk S, Thybusch B (1992) Sorption of uranyl ions on hydrous silicon dioxide. *Radiochim Acta* 57:45–50
- Liu J, Feng X, Fryxell GE, Wang LQ, Kim AY, Gong M (1998) Hybrid mesoporous materials with functionalized monolayers. *Adv Mater* 10:161–165
- Mangrulkar PA, Kamble SP, Meshram J, Rayalu SS (2008) Adsorption of phenol and *o*-chlorophenol by mesoporous MCM-41. *J Hazard Mater* 160:414–421
- Michard P, Guibal E, Vincent T, Le Cloirec P (1996) Sorption and desorption of uranyl ions by silica gel: pH, particle size and porosity effects. *Micropor Mater* 5:309–324
- Mirjalili K, Roshani M (2007) Resin-in-pulp method for uranium recovery from leached pulp of low grade uranium ore. *Hydrometallurgy* 85:103–109
- Nakajima A, Sakaguchi T (1999) Recovery of uranium from uranium refining waste water by using immobilized persimmon tannin. *J Radioanal Nucl Chem* 242:623–626
- Nascimento MRL, Fatibello-Filho O, Teixeira LA (2004) Recovery of uranium from acid mine drainage water by ion exchange. *Miner Process Extr Metall Rev* 25:129–142
- Schmeide K, Pompe S, Bubner M, Heise KH, Bernhard G, Nitsche H (2000) Uranium(VI) sorption onto phyllite and selected minerals in the presence of humic acid. *Radiochim Acta* 88:723–728
- Sepehrian H, Ahmadi SJ, Waqif-Husain S, Faghihian H, Alighanbari H (2010) Adsorption studies of heavy metal ions on mesoporous aluminosilicate, novel cation exchanger. *J Hazard Mater* 176:252–256
- Shin YS, Burleigh MC, Dai S, Barnes CE, Xue ZL (1999) Investigation of uranyl sorption on mesoporous titanium-based sorbents. *Radiochim Acta* 84:37–42
- Singh SK, Dhama PS, Tripathi SC, Dakshinamoorthy A (2009) Studies on the recovery of uranium from phosphoric acid medium using synergistic mixture of (2-Ethyl hexyl) Phosphonic acid, mono (2-ethyl hexyl) ester (PC88A) and Tri-*n*-butyl phosphate (TBP). *Hydrometallurgy* 95:170–174
- Song Y, Wang Y, Wang L, Song C, Yang ZZ, Zhao A (1999) Recovery of uranium from carbonate solutions using strongly



- basic anion exchanger 4: column operation and quantitative analysis. *React Funct Polym* 39:245–252
- Tsuruta T (2002) Removal and recovery of uranyl ion using various microorganisms. *J Biosci Bioeng* 94:23–28
- Zhang Z, Clifford DA (1994) Exhausting and regenerating resin for uranium removal. *J Am Water Works Assoc* 86:228–241

