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Particulate Science and Technology: An International Journal

Publication details, including instructions for authors and subscription information:
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Accepted author version posted online: 08 Jan 2013. Published online: 24 May 2013.

To cite this article: Ali Malekynejad, Hamid Sepehrian & Mahbobeh Manoochehri (2013): Adsorption of Thorium from Aqueous Solution using Nanoporous Adsorbents: Effect of Contact Time, pH, Initial Concentration, and Temperature, Particulate Science and Technology: An International Journal, 31:4, 372-378

To link to this article: http://dx.doi.org/10.1080/02726351.2013.763880

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Particulate Science and Technology, 31: 372–378
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ISSN: 0272-6351 print/1548-0046 online
DOI: 10.1080/02726351.2013.763880

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Adsorption of Thorium from Aqueous Solution using Nanoporous Adsorbents: Effect of Contact Time, pH, Initial Concentration, and Temperature

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Nanoporous silicates MCM-41 have been prepared using different surfactants such as cetyltrimethylammonium bromide (C_{16}TAB) and dodecyltrimethylammonium bromide (C_{12}TAB) as template. The adsorbents are characterized using powder x-ray diffraction, nitrogen adsorption-desorption isotherm data, scanning electron microscopy, and transmission electron microscopy. The thorium sorption was studied as a function of shaking time, pH, initial concentration, and temperature. The sorption of thorium at the determined optimum conditions follows Langmuir and Freundlich isotherms. The results show that the nanoporous MCM-41 synthesized by C_{12}TAB has more adsorption capacity than the MCM-41 synthesized by C_{16}TAB (77.6 $\mu mol \cdot g^{-1}$ vs. 52.1 $\mu mol \cdot g^{-1}$) at 25°C. Th(IV) adsorption onto nanoporous adsorbents was very fast process and therefore, this adsorbent is suitable for column separation. Thermodynamic parameters such as ΔH°, ΔS° and ΔG° were found to be 47.76 $KJ \cdot mol^{-1}$, 196.21 $J \cdot mol^{-1} \cdot K^{-1}$, and 19.00 $KJ \cdot mol^{-1}$, respectively (at 298 K). The positive value ΔH° suggested the endothermic nature of adsorption and negative ΔG° indicates the feasibility and spontaneity of the adsorption process.

Keywords: Adsorption behavior, MCM-41, nanoporous, thorium

1. Introduction

The long-live radionuclides (such as uranium and thorium) in radioactive waste have considered to be dangerous pollutants and their migration in groundwater is strongly affected by adsorption on the geologic materials (Kaygun and Akyil 2007).

Thorium is a naturally occurring, slightly radioactive metal. It is estimated to be about three to four times more abundant than uranium in the Earth's crust. Some human activities such as exploitation of ores with associated thorium and nuclear fuel reprocessing can also concentrate this element (Salinas-Pedroza and Olguin 2004). Since last century, thorium has been extensively used in a variety of applications. These applications produce various gaseous, liquid and solid wastes containing isotopes of uranium, thorium and the daughter ions of Rn, Po, Bi, Ra. Liquid wastes are freed into the surface or the ground waters of mines (Kaygun and Akyil 2007).

A number of methodologies including evaporation, chemical precipitation, ion exchange, and adsorption have been developed to remove thorium from aqueous solutions (Hu et al. 2010). Among these methods, adsorption is one of the most widely used one in nuclear/radiation chemistry (Rojo et al. 2009; Talip et al. 2009; Tan et al. 2009). In recent years, the adsorption of Th(IV) on different adsorbents was studied extensively(Chen and Wang 2007; Tan et al. 2007; Zhao et al. 2008; Chen and Gao 2009; Bursali et al. 2010; Qian et al. 2010).

The discovery of nanoporous materials (Beck et al. 1992) with large surface area and uniform pores, wide opened a new approach for the removal/entrapment of persistent inorganic pollutants (Feng et al. 1997; Liu et al. 1998; Fryxell et al. 1999; Shin et al. 1999). MCM-41 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 (Kresge et al. 1992; Selvam et al. 2001). The characteristic of nanoporous silicates suggest potential applications in the fields of adsorption, catalysis, and nanotechnology due to the large specific surface area and regular porosity (Cheng et al. 1997; Jal et al. 2004).

In this article, the adsorption studies of thorium on nanoporous silicate MCM-41 are reported. The adsorption isotherm, adsorption kinetics, adsorption thermodynamic, and pH effect have also been studied in detail.

2. Experimental

2.1 Materials

All the chemicals used were of analytical grade from Merck (Darmstadt, Germany), except cetyltrimethylammonium

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bromide (C_{16}TAB) and dodecyltrimethylammonium chloride (C_{12}TAB) which was supplied by Aldrich (UK).

2.2 Preparation of Nanoporous Silicate MCM-41

The nanoporous MCM-41 samples were prepared by mixing sodium silicate as silicon source, and a cationic surfactant as template. In a typical procedure, surfactant was dissolved in deionized water, and was stirred for 15 min, after that sodium silicate was added and it was further stirred for 30 min. The pH value was adjusted at 9 by adding sulfuric acid ($2\,mol \cdot L^{-1}$). After 4 h stirring, the resulting gel was transferred to a teflon-steel autoclave and was left for 72 h at 373 K. Finally, white precipitate was filtered, washed five times with deionized water, and dried in air oven at 323 K for 24 h. The material was calcined at 813 K for 6 h. Two molar compositions were used as follows:

1: 0.29 Na_2O: 0.53 C12TAC: 1 SiO_2: 100 H_2O
2: 0.29 Na_2O: 0.12 C16TAB: 1 SiO_2: 100 H_2O.

The samples prepared were labeled as follows: CX-MCM-41 where MCM-41 (Mobil Composition of Matter) indicated hexagonal ordered nanoporous silicate and CX indicated the surfactant used (C16 and C12 show C16TAB and C12TAB surfactants, respectively).

2.3 Characterization

A Philips (the Netherlands) X'pert powder diffractometer system with Cu-Kα (λ=1.541 Å) r adiation was used for x-ray studies. X-ray diffraction (XRD) analysis was performed from 1.5° (2θ) to 10.0° (2θ) at a scan rate of 0.02° (2θ).sec^{-1}. Nitrogen adsorption studies were made with a Quantachrome NOVA 2200e instrument. Nitrogen adsorption 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 data (Brunauer et al. 1938). The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951). The scanning electron micrographic image was recorded using a philips microscope. Transmission electron microscopy (TEM) image was taken by JEM-1200 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 (ICP) of Varian Liberty 150-Axial (USA). A water-bath shaker model CH-4311 (Infors AG, Germany) was used in determination of distribution coefficients.

2.4 Procedure for Adsorption Studies

Adsorption studies of the thorium ion on the MCM-41 adsorbents were carried out using batch method. In this procedure, 100 mg of adsorbent material were added to a 10 mL buffered solution of 5–250 $mg \cdot L^{-1}$ thorium ions. The pH of the solution was adjusted with sodium hydroxide and hydrochloric acid. The suspension was stirred for preselected period of time using a water shaker bath. Then it was filtered and the amount of thorium ion was determined by ICP. The sorption rate (%), the sorption concentration (q, $mol \cdot g^{-1}$) and the distribution coefficient (K_d, $mL \cdot g^{-1}$) were calculated using the relationships

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

$$q\,(mol \cdot g^{-1}) = (C_i - C_f) \times \frac{V}{m} \quad (2)$$

$$K_{eq}\,(m \cdot g^{-1}) = \frac{(C_i - C_f)}{C_f} \times \frac{V}{m} \quad (3)$$

where m is the mass of adsorbent; V is the volume of thorium aqueous solution contacted with adsorbent (mL); C_i is the initial concentration of thorium ($mg \cdot L^{-1}$); and C_f is the equilibrium concentration of thorium after sorption ($mg \cdot L^{-1}$).

2.5 Effect of pH

The effect of solution pH on the adsorption behavior was determined at a constant temperature of 25°C. In batch experiments, 100 mg of the MCM-41 adsorbents were equilibrated with 10 mL of the buffer solution containing 20 $mg \cdot L^{-1}$of thorium ions at various pHs for 5 h.

2.6 Kinetic Study

In a typical kinetics test, 100 mg of the adsorbents were added to 10 mL of 20 $mg \cdot L^{-1}$ of thorium solution at selected pH. The suspension was agitated for different periods of time (0.5–16 h) using a water-bath shaker.

2.7 Adsorption Isotherm

In several batch experiments, 100 mg portions of the MCM-41 adsorbents were equilibrated with varying concentrations of thorium ion (initial concentration range from 5 to 250 $mg \cdot L^{-1}$) at selected pH. The suspensions were agitated for 5 h using a water-bath shaker. Then, the supernatant solutions were removed and filtered. The concentrations of thorium ion (F, $\mu mol \cdot L^{-1}$) in solution were determined with ICP and the amounts of adsorbed thorium on adsorbent (B, $\mu mol \cdot g^{-1}$) were calculated from these values. Among various binding models, Langmuir and Freundlich isotherms have been frequently employed to describe experimental data of adsorption isotherms. The Langmuir adsorption isotherm is mathematically expressed as;

$$B = \frac{K_l(q_{\max})F}{1 + K_l F} \quad (4)$$

where B ($\mu mol \cdot g^{-1}$) is the amount of analyte bound to adsorbent; F (μM) is the equilibrium concentration of adsorbate in solution; q_{max} is the maximum adsorption capacity ($\mu mol \cdot g^{-1}$); and K_l is the constant for a given adsorbate and adsorbent at different temperatures. The Langmuir equation is the most common model employed to describe the adsorption process in homogenous systems.

For comparative purposes the experimental data have been fitted to the well-known Freundlich equation:

$$B = K_f F^m \quad (5)$$

where K_f and m are constants for a given adsorbate and adsorbent at different temperatures.

2.8 Thermodynamic Study

The effect of temperature on the adsorption characteristics was investigated by determining the adsorption at different temperature (298–328 K). Thermodynamic parameters of adsorption have been determined using classical thermodynamic equations.

The equations given below were used to evaluate the values of ΔH°, ΔS° and ΔG°.

$$LnK_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

And

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

ΔH° and ΔS° can be determined from the slope and the intercept of the linear plot of LnK_{eq} versus $1/T$.

3. Result and Discussions

3.1 XRD Analysis

The XRD patterns of the calcined C12-MCM-41 and C16-MCM-41 are presented in Figure 1. The XRD patterns of samples show a strong diffraction at 2θ smaller than 3° along with presence of small peaks that confirms the formation of nanoporous MCM-41(Beck et al. 1992).This result is characteristic of hexagonal pore structure of MCM-41.

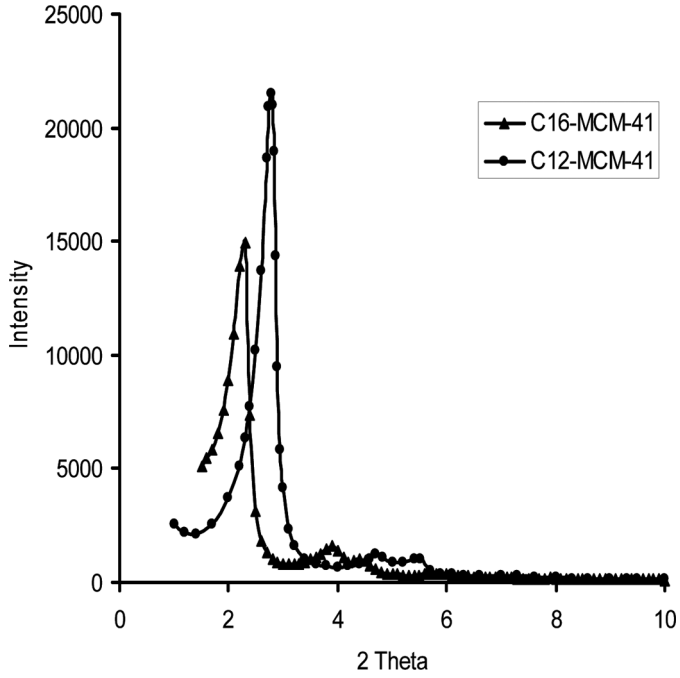


Fig. 1. XRD patterns of the C16-MCM-41 (calcined) and C12-MCM-41 (calcined).

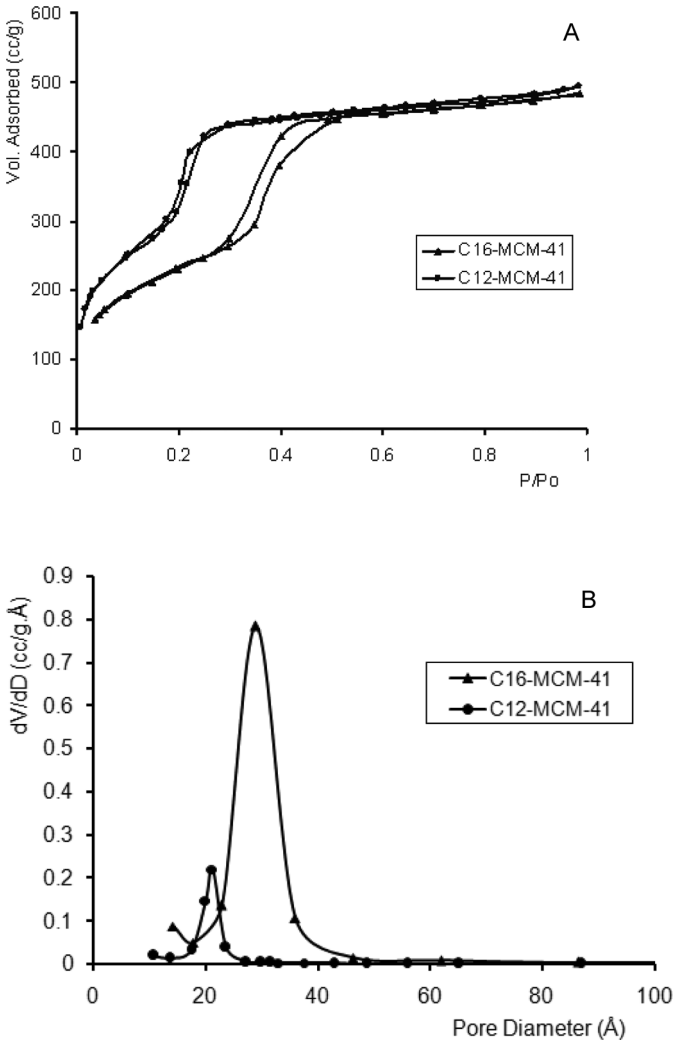


Fig. 2. (A) Nitrogen adsorption/desorption isotherms and (B) pore size distribution for C16-MCM-41 and C12-MCM-41.

3.2 Nitrogen Sorption Isotherms

The nitrogen adsorption isotherms and corresponding pore size distribution of the C12-MCM-41 and C16-MCM-41 are given in Figure 2. N_2 adsorption-desorption isotherms for C12-MCM-41 and C16-MCM-41 showed a typical IV-type adsorption profile consisting of a condensation due to the formation of mesopores (Figure 2). The mode of preparation has a significant effect on the size and shape of the cavities, pore volume and surface area of the adsorbents as given in Table 1. The MCM-41 sample synthesized by C12 surfactant has larger surface area (1395 vs. 1300 m^2/g) and smaller pores diameter (21 vs. 29 Å). This difference is due to difference in alkyl chain length of surfactants.

3.3 Scanning Electron Micrographs

The scanning electron microscope (SEM)images of the C12-MCM-41 and C16-MCM-41 samples are given in

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Table 1. Physical characteristics of C16-MCM-41 and C12-MCM-41

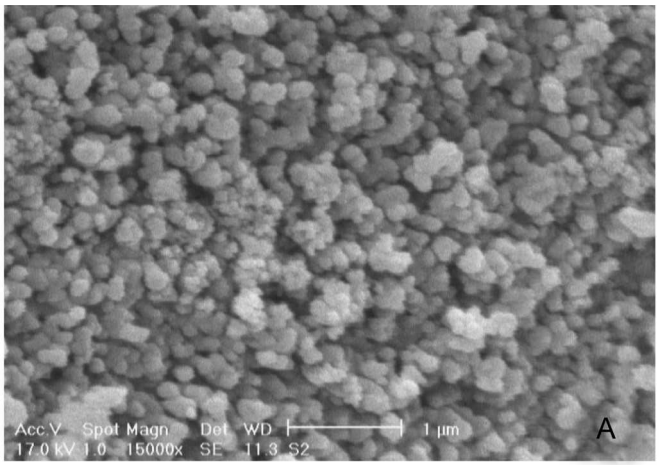
Adsorbent	XRD d_{100} (Å)	Unit cell parameter[a] (a_o) (Å)	Pore volume (cc/g)	BET surface area (m^2/g)	Pore diameter (Å)
C16-MCM-41	39.8	46.0	1.30	1303	29.0
C12-MCM-41	31.9	36.8	0.89	1395	21.3

[a]Calculated from the equation $a_\circ = 2d_{100}/\sqrt{3}$.

Figure 3A and 3B, respectively. The SEM images exhibit uniform spherical crystallites.

3.4 Transmission Electron Micrographs

TEM of the C12-MCM-41 and C16-MCM-41 samples are given in Figure 4A and 4B, respectively. The TEM images show that the pore diameter of the channels calculated from N_2 sorption measurement of the C12-MCM-41 and C16-MCM-41 samples are about 20 and 30 Å, respectively.



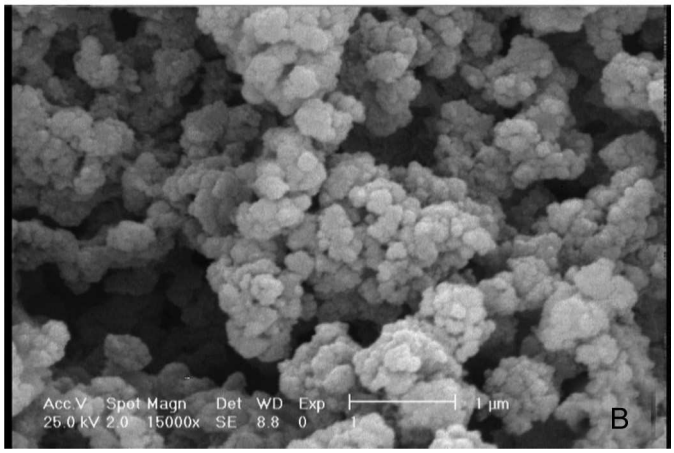
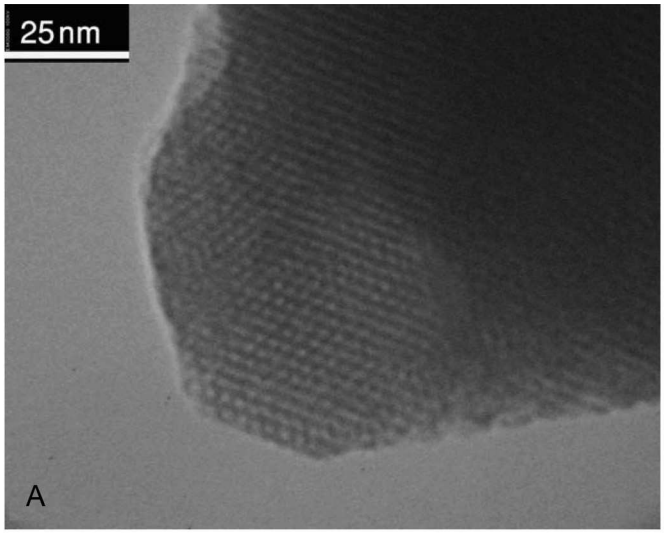


Fig. 3. SEM of (A) C12-MCM-41 and (B) C16-MCM-41 samples.



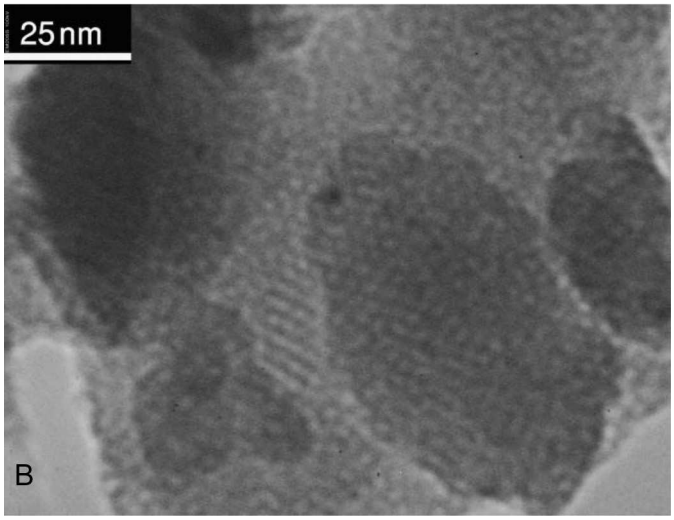


Fig. 4. TEM of (A) C12-MCM-41 and (B) C16-MCM-41 samples.

3.5 Effect of pH

The effect of pH on the sorption of thorium was studied from pH 1 to 5. As seen in Figure 5, the adsorption of thorium varied significantly with the pH of solution. When $pH \leq 2.0$, Th^{4+} 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 $pH < 2.0$, it was found that thorium showed no adsorption toward MCM-41. After $pH > 2$ with an increase in basicity of the aqueous solution, $Si - OH_2^+$ as a cation gradually converted to a nautral Si-OH by reacting with OH^-, While Th^{4+} gradually hydrolyzed to $ThOH^{3+}$ and $Th(OH)_2^{2+}$ by connecting with OH^-. Since $ThOH^{3+}$ and $Th(OH)_2^{2+}$ were complexible species with the neutral Si-OH, so, thorium showed the adsorption towards MCM-41 adsorbent with an increase in pH value. The strong adsorption of Th(IV) on MCM-41 is attributed to surface complexation or strong chemical adsorption (Xu et al. 2005; Hu

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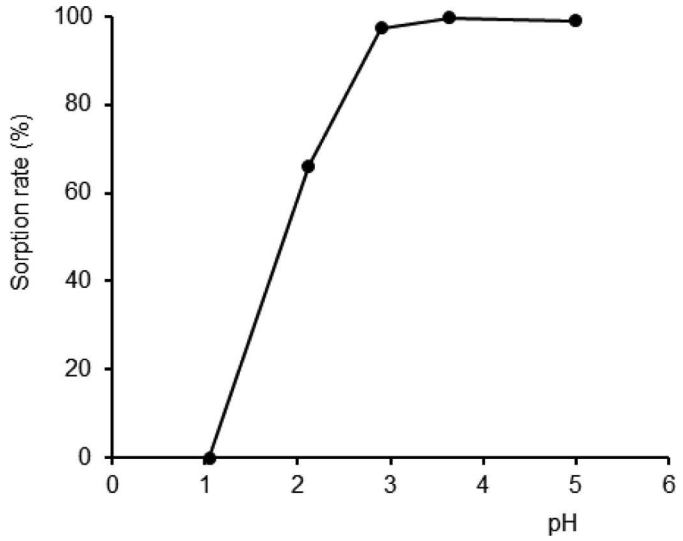


Fig. 5. Effect of pH on adsorption of thoriumonto the MCM-41 adsorbent.

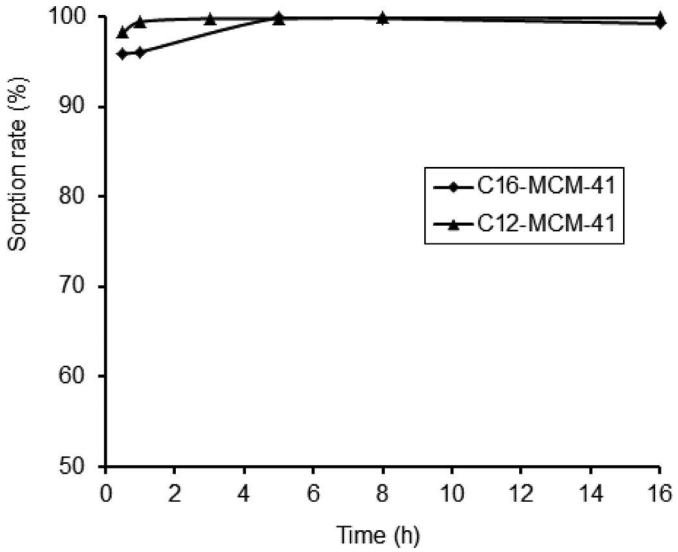


Fig. 6. Effect of contact time on adsorption of thoriumonto the C16-MCM-41 and C12-MCM-411 adsorbents at 298 K, pH = 3.6 and $C_0 = 20\,\mu g \cdot mL^{-1}$.

et al. 2009; Chang et al. 2007; Zhang et al. 2006; Yu et al. 2006; Yu et al. 2007). It is also necessary to note that the high adsorption of Th(IV) on MCM-41 may also result in the precipitation of Th(IV) on MCM-41. For example, at pH 3.8, nearly 100%Th(IV) is adsorbed on MCM-41, surface adsorbed Th(IV) can form precipitation at lower pH because of the high local concentration of Th(IV) on MCM-41 surface. The local high concentration of Th(IV) on MCM-41 surface may lead to the precipitation of Th(IV) on MCM-41 surfaces(Yang et al.. 2009; Zhang et al. 2010). The next experiments in this study were carried out at natural pH (3.6).

3.6 Effect of Shaking Time

The sorption of Th(IV) ions has been investigated onto the adsorbents as a function of shaking time in the range of 0.5 to 16 h. the results are given in Figure 6. As seen from Figure 6, the sorption yield slightly increases with increasing shaking time and attains equilibrium as 98.2% sorption within 30 min. The fast adsorption 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 thorium ions transportation in the process. Fast adsorption rate in nanoporous adsorbents show that this adsorbents are suitable for column separation rather than other adsorbents (Zuo et al. 2011).

3.7 Adsorption Isotherm

The adsorption isotherms of Th(IV) on C16-MCM-41 and C12-MCM-41 at 25, 35, and 55°Care plotted in Figure 7A and 7B. One can see that the adsorption isotherm is high at 55°C and is low at 25°C. The results indicate that high temperature is favorable for Th(IV) adsorption onto MCM-41, the results are similar to Th(IV) adsorption to

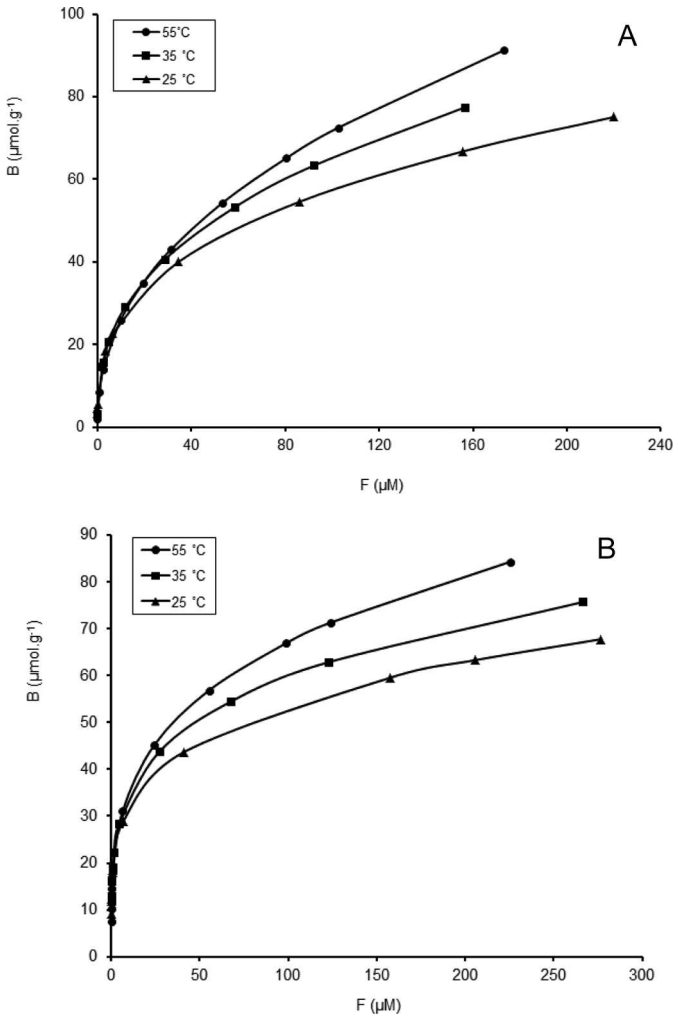


Fig. 7. Experimental adsorption isothermsfor (A) C12-MCM-41 and (B) C16-MCM-41.

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Table 2. Fitting parameters of adsorption model isotherms

	Fitting parameters						
		Langmuir			Freundlich		
Adsorbents	T (°C)	R^2	K_l (L μmol^{-1})	q_{max} (μmol g^{-1})	R^2	K_f (μmol g^{-1} mM^{-1})	m
C16-MCM-41	25	0.791	0.72	52.1	0.977	22.59	0.20
	35	0.966	0.42	53.8	0.995	19.82	0.23
	55	0.916	0.12	67.1	0.986	18.50	0.27
C12-MCM-41	25	0.989	0.05	77.6	0.995	11.99	0.35
	35	0.977	0.04	84.7	0.997	11.35	0.39
	55	0.964	0.03	86.2	0.988	9.45	0.43

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zeolitic volcanic tuff and mesoporous Al-MCM-41(Zuo et al. 2011; Humelnicu et al. 2006).

The equation constant values q_{max}, K_l, K_f and m, calculated from the experimental data (Table 2). The parameters values presented in Table 2 show that Freundlich model best fitted to the experimental data. The parameter $m = 1/n < 1$ represents a favorable sorption of thorium cations and also indicate a multilayer adsorption.

Comparison of adsorption capacities of the nanoporous MCM-41 adsorbents (0.05–0.09 mmol · g^{-1}) with other adsorbents such as PAN/zeolite composite (0.04 mmol · g^{-1}) show that the nanoporous MCM-41 (especially C12-MCM-41) is better adsorbent for Th(IV) adsorption.

3.7.1 *Determination of Thermodynamic Parameters*

Temperature is an important parameter that dominates the physicochemical behavior of metal ions in the environment. Figure 8 show linear plots of LnKeq versus 1/T for thorium adsorption onto the C16-MCM-41 and C12-MCM-41 adsorbents. The thermodynamic data calculated by Equation (6) and (7) are listed in Table 3. A positive value of the standard enthalpy change (ΔH°) proves that the adsorption process of Th(IV) is endothermic. It is supported by the obvious increasing adsorption with the rise of temperature. For Th(IV) ions to get across the solution and to reach the adsorption sites, it is necessary for them firstly to be divested out of their hydration shell, and this process needs the import of energy. If the exothermicity combined with the adsorption of Th(IV) onto Al-MCM-41 is not in excess of the dehydration energy of Th(IV) ions, the entire energy balance will result in the endothermic behavior (Zuo et al. 2011). It is also concluded that the driving force for thorium adsorption must come from an entropy effect.

The Gibbs free energy change (ΔG°) is negative as expected for a spontaneous process under the experimental conditions. The more negative value of ΔG° suggests more efficient adsorption of Th(IV) with the rise of temperature. The positive values of ΔS° reflect the affinity of MCM-41 toward Th(IV) ions in aqueous solutions and may indicate some changes of the structure in adsorbent (Zuo et al. 2011).

The ΔG° values up to −20 kJ · mol^{-1} are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while $\Delta G°$ values more negative than −40 kJ · mol^{-1} involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond (chemical adsorption). The $\Delta G°$ values obtained in this study for thorium are about −20 kJ · mol^{-1}, which indicates that physical adsorption is the predominant mechanism in the sorption process.

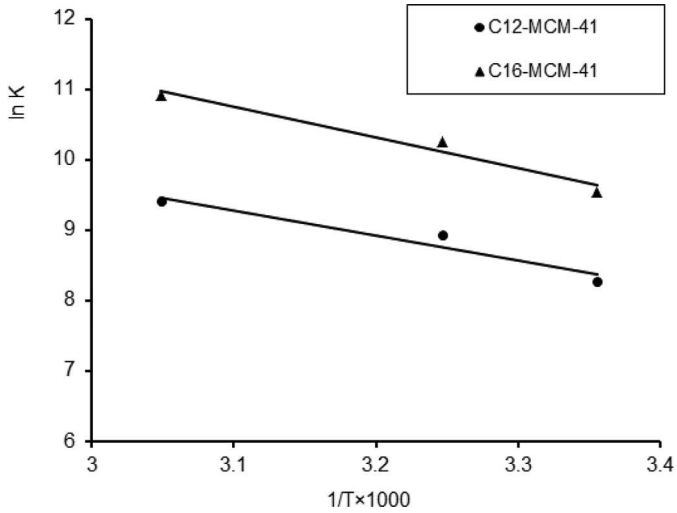


Fig. 8. The plotsof LnK_{eq} versus 1/T for adsorption data of thorium onto C16-MCM-41 and C12-MCM-41 adsorbents.

Table 3. Thermodynamic parameters for the adsorption of thorium on the adsorbents

Adsorbents	T (°C)	ΔH° (kJ · mol^{-1})	ΔS° (J · mol^{-1} · K^{-1})	ΔG° (kJ · mol^{-1})
C16-MCM-41	25	57.57	266.30	−21.78
	35			−24.44
	55			−27.11
C12-MCM-41	25	47.76	196.21	−19.00
	35			−21.24
	55			−23.48

4. Conclusion

The adsorption behavior of Th(IV) onto the synthesized nanoporous MCM-41 adsorbents was investigated. It was found the nanoporous MCM-41 exhibited an excellent adsorption selectivity for Th(IV). The temperature variation has been used to evaluate the values of ΔH°, ΔS° and ΔG°. The positive values of ΔH° and negative ΔG° indicate endothermic and spontaneous nature of sorption, respectively and the driving force for thorium adsorption must come from an entropy effect. Fast adsorption rate in nanoporous adsorbents show that these adsorbents are suitable for column separation.

Acknowledgment

The authors are thankful to analytical chemistry laboratories for some laboratory facilities.

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