Solid Phase Extraction of Thorium and Uranium and their Separation from Lanthanides using Humic Acid Silica Gel as a Low-Cost Adsorbent

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Abstract. Solid phase extraction and separation of thorium (Th), uranium (U) and lanthanides were achieved using a humic acid-modified silica gel (Si-HA). Adsorption capacity, effect of contact time, pH, and adsorbent dose were examined at room temperature. The maximum adsorbent capacities (pH = 3) for Th and U were 28.0 and 31.3 mg g^{-1}, respectively. The isotherm parameters denoted that the adsorption was favorable and optimum conditions were attained within 90 min. The kinetic data conformed well to pseudo-second order and intra-particle diffusion models. The distribution coefficients of U, Th and lanthanides in EDTA, citric acid and nitric acid media signify the possible separation of each element from the others. The salinity did not significantly affect the ability of Si-HA to extract Th and U. The adsorbent stability and reusability were also assessed through four-adsorption-desorption cycles. The simplicity of the proposed separation method along with the stability of the adsorbent and high regeneration efficiency under acidic conditions demonstrated the merit of using Si-HA as a low-cost adsorbent.

1   Introduction

Thorium (Th) and uranium (U) are radioactive elements that are closely associated with lanthanides in nature, e.g. monazite and bastnaesite minerals [1]. Since lanthanides are essential elements in modern technology, a separation technique to remove Th and U from lanthanides is important not only in terms of environmental restoration but also in hydrometallurgy and nuclear fuel treatments [2]. Among the methods that have been proposed for the extraction and recovery of these elements, solid phase extraction with the use of an

adsorbent has advantages because of its ability to address low metal and pollutant concentrations, e.g. radioactive waste [3].

Various adsorbents have been investigated for their ability to pre-concentrate Th and U, as described by Donia, *et al.* and Nilchi, *et al.* in [4,5], but reports describing their recovery and separation from lanthanides are still very limited. Furthermore, many materials investigated are not cost-effective because of the use of expensive and not widely available chemicals. A complicated preparation procedure also hinders material application at larger scale. Humic acid on the other hand offers a solution to these problems since it is inexpensive and widely available and can bind metal elements. Unfortunately, the applicability of humic acid is hindered by the difficulty of separating it from the liquid phase. This problem can be overcome by attaching humic acid molecules to stable and larger inorganic or organic particles as support, e.g. a silica gel [6].

A silica gel modified with humic acid (Si-HA) has been used to study the binding interaction between humic acid and metal ions, as described by Patel, *et al.*, Prado, *et al.*, Stathi and Deligiannakis in [7-9]. However, its applicability for recovering Th and U, including their separation from lanthanides, remains unknown. In this study, we examined the feasibility of Si-HA for the pre-concentration and separation of Th, U and lanthanides through the following experiments: 1) solid phase extraction of Th, U and lanthanides by Si-HA from an aqueous solution as a function of the acidity, metal concentrations, contact time and salinity; 2) recovery and separation of Th and U from lanthanides retained by Si-HA; and 3) reusability studies to assess the stability and economic merit of the adsorbent. The adsorption capability was evaluated at high salinity because Th and U are sometimes associated with placer beach deposits [10].

2   Materials and Method

2.1   Instrumentation and Chemical Reagents

The pH was measured with an F-52 Horiba pH meter. Elemental analysis of the mixture solution was performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (SPS-7700, Seiko Instruments). Individual solutions were analyzed spectrophotometrically using Arsenazo III (Alfa Aesar, USA) as the chromogenic reagent. Thorium nitrate and uranyl nitrate hexahydrate salts (Wako Chemical, Japan) as well as lanthanide (La, Nd, Dy and Yb) ICP standard solutions (1000 mg L^{-1}) provided by Cica-Merck, Japan, were used to prepare stock solutions. All dilutions were performed using purified water (Milli-Q system, Millipore). Commercial humic acid provided by ACROS Organic USA was purified according to Koopal, *et al.* in [11]. Other

chemicals used in the experiments were of analytical grade and used without further purification.

2.2　Adsorbent Preparation

The silica gel modified by humic acid (Si-HA) used in this study was prepared using a modification of the procedure described by Prado, *et al.* in [8] as follows. Twenty grams of activated silica gel (particle size 40-63 µm) was suspended in 100 mL of dry toluene. 3-Aminopropyltrimethoxysilane (20 mL) was added to this suspension and fluxed at 140 °C for 72 hours to produce a Si-NH_2 suspension. The suspension was separated and washed with water and dried at 50 °C. One gram of Si-NH_2 was suspended in 30 mL of 0.1 M sodium hydroxide containing 300 mg of the purified humic acid (pH 7.5) and stirred for 20 hours at room temperature to produce a Si-HA suspension. The suspension was separated and washed with a 0.2 M sodium chloride solution at pH 10, then with 1 mM hydrochloric acid and finally dried at 120 °C for 24 hours.

2.3　Optimum Conditions by Batch Adsorption Experiments

Batch experiments of metal ion adsorption onto Si-HA were carried out to elucidate the optimum conditions for adsorption by varying the pH, analyte concentration, contact time and salinity, as well as to test the regeneration or reusability of the Si-HA adsorbent. In the batch method, typically, 50 mg of Si-HA is equilibrated with 25 mL of a metal solution by stirring at 500 rpm at room temperature. Preliminary experiments showed that equilibrium was attained within 3 hours. The supernatant solution was separated by centrifugation and the metal ion concentration in the aqueous phase (C_E) was analyzed using a spectrophotometer or ICP-AES. The adsorption capacity (q, mg g^{-1}) was calculated by the equation $q = (C_i - C_E)V/m$, where C_i (mg L^{-1}), C_E (mg L^{-1}), V (mL) and m (mg) are metal ion initial concentration, metal ion concentration at equilibrium, aqueous phase volume, and added adsorbent weight, respectively. The adsorption recovery was determined with the equation $R = (C_i - C_E)/C_E$. In the reusability studies, Th or U adsorbed by Si-HA was recovered using 10 mL of 1 M or 2 M nitric acid. Before being reused in the next sorption process, the adsorbent was washed thoroughly using doubly distilled water and dried at 50 °C.

2.4　Separation Studies by Batch Experiments

The feasibility of the recovery and separation of Th, U and lanthanides was studied in batch experiments by adsorption and desorption processes. In the adsorption process, 50 mg of Si-HA was stirred with 25 mL of a Th, U and lanthanides mixture solution (each initial concentration was 2 mg L^{-1}) over a pH range from 0.5 to 6.0 to clarify the pH effect on the separation. In the desorption

experiments, 2 mL of leaching solutions at varied concentrations was introduced to 25 mg of a Si-HA adsorbent containing a mixture of Th, U and lanthanides (each metal content was 1 mg g^{-1}). The leaching solutions tested were hydrochloric acid (0.1-4 M), EDTA (0.1-10 mM) and citric acid (1-10 mM).

The viability of the separation of two metal ions is predicted by their separation factor ($\alpha = D_1/D_2$), where D_1 and D_2 refer to the first and second metal ion distribution coefficients ($D= C_S/C_L$, where C_L (mg L^{-1}) and C_S (mg g^{-1}) are the metal concentrations in the supernatant solution and metal concentration in the adsorbent, respectively.

3   Results and Discussion

3.1   Effect of Acidity on Adsorption

The effect of initial pH on the adsorption of thorium and uranyl ions is shown in Figure 1(a). Thorium required a pH higher than 1.5 for optimum adsorption. Uranium ions were quantitatively retained at a pH higher than 3, while lanthanides (La, Nd, Dy and Yb) required a slightly acidic to neutral pH (Figure 1(b)). At a lower pH, low adsorption was due to the electrostatic repulsion between the protonated ligand sites (carboxylic and phenolic) and ions with the same charge. As the pH increased, the ligand sites became deprotonated into negatively charged functional groups, which attract positive target ions in the aqueous phase.
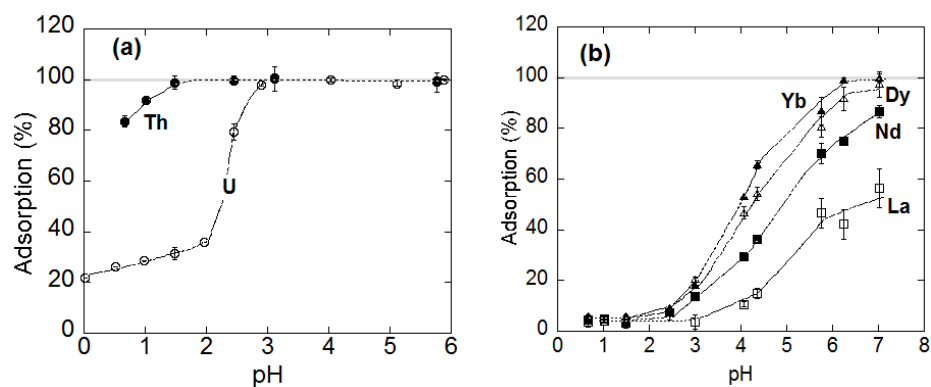

Figure 1 Influence of the initial pH on metal adsorption onto the Si-HA adsorbent (a) U and Th; (b) La, Nd, Dy and Yb.

3.2   Adsorbent Capacity and Isotherm

Adsorption was described by the isotherm functions of the quantity of the adsorbate on the adsorbent, e.g. the Langmuir and Freundlich models. Figure 2a shows the adsorption by the Si-HA adsorbent according to the Langmuir model ($C_E/q_E = C_E/q_{max} + 1/Kq_{max}$), where C_E, q_E, q_{max} and K are the equilibrium concentration (mg L^{-1}) adsorption capacity at equilibrium (mg g^{-1}), adsorption maximum capacity (mg g^{-1}) and binding constant value (L mg^{-1}), respectively. The Freundlich adsorption isotherm model ($\log q_E = \log K_F + 1/n \log C_E$; Figure 2b) was applied to determine the Freundlich constant, which relates to the capacity (K_F) and intensity of adsorption ($1/n$).

The Langmuir and Freundlich parameters and root mean square error (*RMSE*) of this study are listed in Table 1. The *RMSE* equation is given by Negrea, *et al.* in [12]. The data were fit to both models. Based on the *RMSE* value, the Freundlich model fit better to the experimental data due to the heterogeneous ligand sites of humic acid. The maximum adsorption capacities (q_{max}) of the six metal ions onto Si-HA were far higher than the values for the unmodified silica gel (Si gel in Table 1).
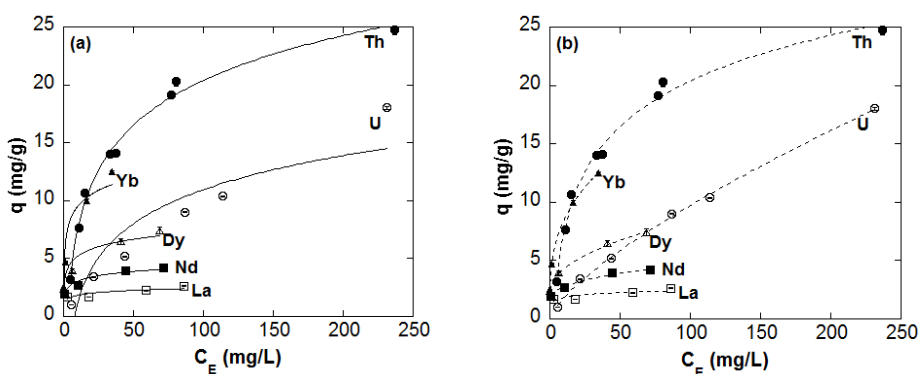
Figure 2 Experimental isotherms for the adsorption of U and Th at pH 3 and lanthanides at pH 6: (a) Langmuir model and (b) Freundlich model.

An intensity of adsorption ($1/n$) value less than 1 signifies the adsorption condition where the adsorbate (metal ion) concentration increases, while the percentage of adsorbed decreases, reaching the saturation capacity. This reflects limited adsorption sites on the adsorbent. Metal species with a lower n value require a higher concentration compared to metal species with a higher n value [13], which is supported by the maximum sorption capacity obtained from the Langmuir or Dubinin-Radushkevich models (Table 1).

The Dubinin-Radushkevich model was used to model the isotherm data based on the equation $q_m = q_{max}e^{[-\beta(RTln(1+1/C_E)^2)]}$, where q_m (mg g^{-1}), q_{max} (mg g^{-1}), C_E (mg L^{-1}), β (mol^2 J^2), R and T (K) are modeled sorption capacity, modeled maximum sorption capacity, equilibrium concentration, free energy of adsorption, gas constant (8.314 J mol^{-1} K^{-1}), and temperature, respectively. To distinguish the type adsorption, Dubinin-Radushkevich adsorption energy Ea (kJ mol-1) was calculated based on the equation $Ea = 1/\sqrt{2\beta}$. Table 1 shows that the adsorption process for all metal species was physical adsorption (Ea < 8 kJ mol^{-1}) [13].

Table 2 shows a list of the maximum adsorption capacity values (q_{max}) of several humic acid-based adsorbents for retaining Th and/or U. Generally, a higher q_{max} was obtained at higher pH condition. Examination of the adsorbent ability to fixate Th and U under acidic conditions would be advantageous because of the general association of Th and U with acidic matrix samples, e.g. mine wastewater and nuclear industry wastewater [15].

**Table 1**   Estimated isotherm parameters for the adsorption of ions onto Si-HA.

Metal ion	pH	Langmuir				Freundlich			Dubinin-Radushkevich		
		q_{max} (mg/g)	Si gel (mg/g)	K (L/mg)	RMSE	n	K_F (L$^{1/n}$/g)	RMSE	q_{max} (mg/g)	E (kJ/mol)	RMSE
U	3	31.3	2.0	0.01	0.46	1.3	0.30	0.22	29.1	0.91	7.21
Th	3	28.0	10.3	0.03	1.81	2.0	2.15	1.72	24.8	2.23	3.47
La	6	2.6	0.2	0.25	0.57	10.0	1.49	0.56	3.2	7.91	1.11
Nd	6	4.3	0.4	0.42	0.59	5.9	1.99	0.44	4.5	7.45	1.20
Dy	6	7.4	0.3	0.40	1.01	4.8	2.94	0.54	7.7	7.07	1.61
Yb	6	12.5	1.3	0.77	1.23	3.6	4.65	0.58	11.5	3.16	1.81

Table 2   Comparison of Th and U Sorption Capabilities of Humic Acid-based Adsorbents from Previous Reports and this Study (q_{max} in mg g^{-1}).

Adsorbent Material	pH	q_{max}		Equilib. time (min)	Reuse. (cycles)	Ref.
		Th	U			
Humic acid on zirconium pillared clay	6		132.7	180	4	[3]
Humic acid-amberlite XAD-4	4	35.0		60		[17]
Insolubilized humic acid	3	20.0	17.0	360		[18]
Humic acid modified silica gel	3	28.0	43.9	180	4	This study

3.3   Adsorption Kinetics

Figure 3 shows that within 15 min the metal removal generally reached 75% of the equilibrium condition. This condition would generally be attained within 90 min. To describe the kinetics of the adsorption process, the experimental data in Figure 3 were treated with pseudo-first order $q_t = q_e(1 - e^{-k_1 t})$, pseudo-second order $q_t = k_2 q_E^2 t / (1 + k_2 q_E t)$ and intra-particle diffusion $q_t = k_i t^{0.5} + I$ models. q_{texp} and q_{tcal} are the sorption capacities based on the experimental data and modeling at a given time, t, respectively, while n is the number of observations. k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}), k_i (mg g^{-1} min$^{0.5}$) and I (mg g^{-1}) are the rate constants of the pseudo-first order, pseudo-second order, intra-particle diffusion rate models and the intra-particle diffusion constant, respectively. While $H = k_2 q_E^2$ (mg g^{-1} min^{-1}) and $t_{1/2} = q_e/H$ (min) are the initial adsorption rate and time required to absorb half of the initial concentration, respectively. The normalized standard deviation (dq) and average relative error (ARE) were used to evaluate the compatibility of the model to the experimental data. dq and ARE given by Weber and Morris in [16].
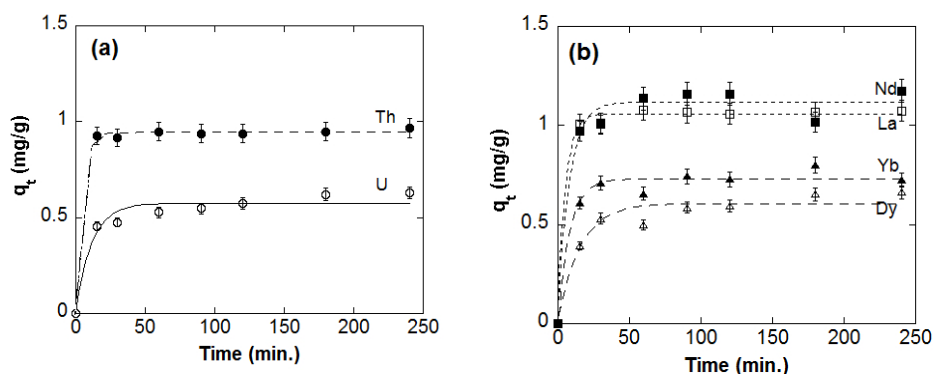
Figure 3 Effect of contact time on the adsorption of (a) Th, U and (b) lanthanide with initial concentration of 2 mg L^{-1}, pH 3 (Th and U) or pH 6 (lanthanides)   at 25 °C.

3.4   Separation Studies by Batch Method

Figure 4(a) shows the distribution coefficients of each metal after a mixture of Th, U and lanthanides (initial concentration for each metal: 2 mg L^{-1}) was subjected to adsorption by the batch method. The result was consistent with the data in Figure 1 and confirmed the favorability of acidic conditions for the separation of Th and U from lanthanides. pH = 3 was the optimum pH to separate Th and U from lanthanides. At this pH, the separation factors of Th–La, Th–Yb, U–La, and U–Yb were 3890, 2930, 50, and 38, respectively.

As shown in Figure 4(b), low separation factors among the metal ion species (0.6-38) indicate that hydrochloric acid is not very useful for separation. EDTA can be used to separate lanthanides from Th and U due to high separation factors (3900 and 195 for Th-La and U-La pairs) at an EDTA concentration of 0.1 mM, as shown in Figure 4(c). Figure 4(d) shows that citric acid was effective at separating U from Th, as was exemplified by the high separation factor between these elements (1.2×10^5 in 1 mM citric acid).

Table 3 Kinetic parameters of Th and U adsorption after fitting with pseudo-first order, pseudo-second order and intra-particle diffusion models.

| Parameters	C_oTh (mg L^{-1})		C_o U (mg L^{-1})		C_o La (mg L^{-1})		C_oYb(mg L^{-1})	
	2	10	2	10	2	10	2	10
Pseudo-first order								
k_1 (min^{-1}) $\times 10^{-3}$	0.27	0.15	0.09	0.49	1.00	1.00	1.00	1.00
q_E model (mg g^{-1})	0.94	3.40	0.57	2.50	1.05	4.57	0.83	4.36
q_E exp.(mg g^{-1})	0.97	3.70	0.63	3.10	1.07	4.79	0.85	4.36
dq (%)	1.55	4.56	8.40	14.25	3.10	6.67	7.11	2.74
ARE (%)	0.02	0.21	0.71	2.03	0.10	0.45	0.51	0.08
Pseudo-second order								
k_2 (g mg^{-1} min^{-1})	2.03	0.09	0.27	0.05	0.76	0.07	0.43	0.44
q_E model (mg g^{-1})	0.95	3.54	0.61	2.89	1.08	4.88	0.88	4.41
q_E exp. (mg g^{-1})	0.97	3.70	0.63	3.10	1.07	4.79	0.85	4.36
H (mg g^{-1} min^{-1})	1.83	1.12	0.10	0.43	0.88	1.61	0.33	8.59
$t_{1/2}$ (min)	0.52	3.16	6.20	6.78	1.23	3.03	2.66	0.51
dq (%)	1.23	4.55	5.26	8.03	1.59	1.91	4.33	2.48
ARE (%)	0.02	0.21	0.28	0.65	0.03	0.04	0.19	0.06
Intra-particle diffusion								
k_i (mg g^{-1} min$^{0.5}$)	0.003	0.063	0.016	0.09	0.01	0.056	0.010	0.000
I (mg g^{-1})	0.91	2.72	0.40	1.77	1.00	4.07	0.74	4.33
dq (%)	0.86	6.43	1.50	3.49	1.96	3.74	4.81	2.71
ARE (%)	0.01	0.41	0.02	0.12	0.04	0.14	0.23	0.07

The high distribution coefficient of Th onto Si-HA in the three leaching agents (Figures 4(a)-(c)) suggests that the three solutions did not effectively recover Th. However, it was found that 1 M nitric acid could desorb Th quantitatively from the Si-HA adsorbent.

3.5   Effect of Salinity

Figure 4 shows that the distribution coefficients of Th, U and lanthanide adsorption in sodium chloride solution varied between 0.05-2 M. Adsorption of

Th and U was insignificantly influenced by salinity, while adsorption of lanthanide was considerably affected. The results signified that beside pH, salinity also contributed to the selectivity of the adsorbent toward Th and U. The decrease of adsorption due to salinity was caused by the formation of less charged chloride species [19], which decrease the electrostatic interaction between the ligand site and target ion.
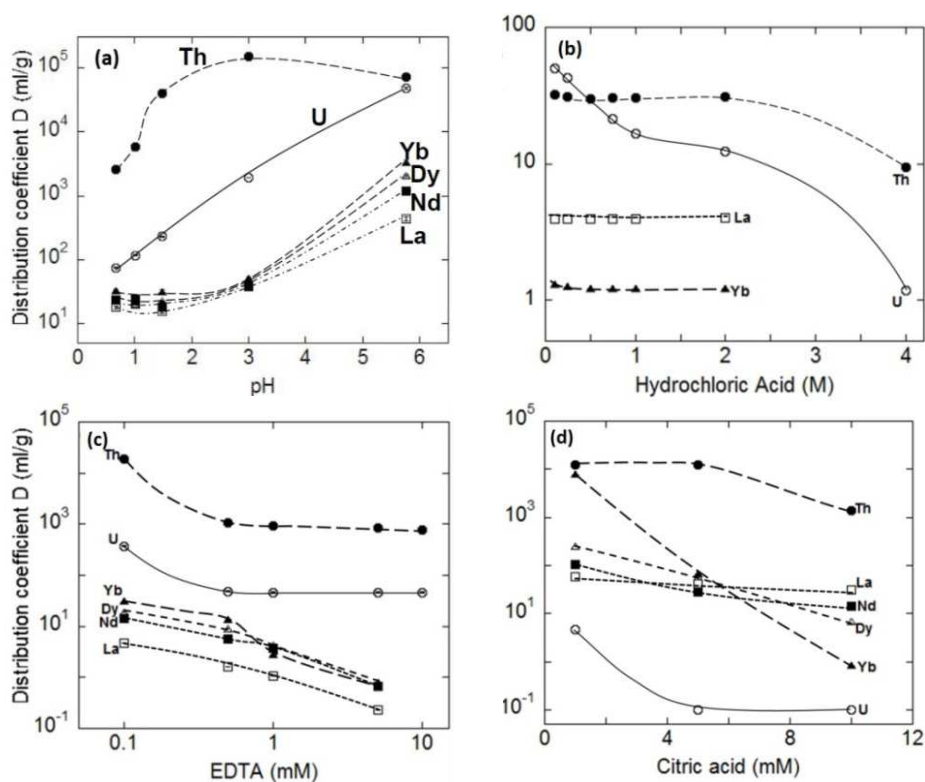
Figure 4 Distribution coefficients of Th, U and lanthanides as a function of (a) pH, after adsorption by Si-HA from the mix solution, and after desorption of Si-HA containing a mixture of Th, U and lanthanides by (b) hydrochloric acid, (c) EDTA and (d) citric acid.
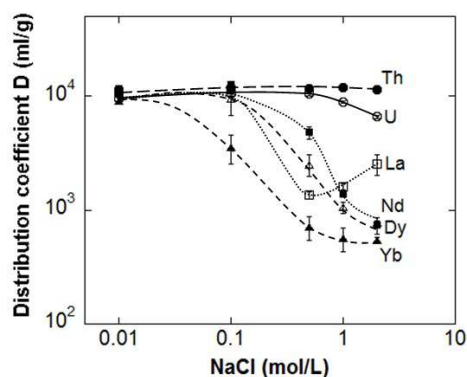
Figure 5 Distribution coefficients of Th, U and lanthanide adsorptions as a function of salinity. Si-HA (10 mg) equilibrated with 5 mL of a metal solution (2 mg L^{-1}).

3.6   Adsorbent Reusability

The reusability evaluation involved a desorption process to regenerate the used adsorbent in order to reuse it in the next cycle of metal adsorption. The regeneration efficiency is the ratio of metal uptake between the first and last runs [4]. After 4 cycles of regeneration using 1 M nitric acid, the regeneration efficiencies for Th and U were found to be 99.6±1.6% and 93.8±5.6%, respectively, while using 2 M nitric acid yielded regeneration efficiencies of 99.1±0.9% Th and 92.6±1.8% U. High regeneration efficiency indicates the stability of the adsorbent in sequential reactions for at least 4 cycles.

4   Conclusions

This study is the first to report humic acid attached to silica gel (Si-HA) as a suitable adsorbent to recover and separate Th and U from lanthanides. The recovery of Th and U was confirmed under acidic conditions (pH 3), while lanthanides required slightly neutral conditions (pH 6). The maximum adsorbent capacities (pH = 3) of Th and U were 28.0 and 31.3 mg g^{-1}, respectively. The kinetic studies denoted that the adsorption of Th, U, and lanthanide ions was favorable and rapid (within 90 min.). The proposed separation method is based on the favored adsorption of Th and U at pH 3 and the differences in the distribution ratios of each metal in EDTA and citric acid. Salinity only slightly affected the adsorbent ability to remove Th and U. The adsorbent showed good stability in strong acid and was reusable for at least 4 cycles. The results affirmed the suitability of the Si-HA adsorbent as an alternative lower-cost adsorbent to recover Th and U, including their separation from lanthanides.

Acknowledgments

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