Adsorption behavior of U(VI)/Th(IV) by acid-leached red mud: A comparative study

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Abstract−Acid-leached red mud, a type of inorganic-adsorptive by-product of bauxite Bayer process via acid leaching, was used for the removal of U(VI)/Th(IV) from aqueous solutions. Variables of the adsorption such as contact time, temperature, solution pH, initial concentration and dose of acid-leached red mud were investigated. The results indicated that the adsorption is strongly affected by dosage, the solution pH, contact time and initial concentration. The isothermal data were fitted with both Langmuir and Freundlich equations, but the data fitted the former better than the latter. A pseudo-first-order kinetic model and pseudo-second-order kinetic model were used to describe the kinetic data, but the pseudo-second-order kinetic model was the better. Thermodynamic parameters such as enthalpy (ΔH^o), entropy (ΔS^o) and free energy change (ΔG^o) were calculated, and the negative ΔG^o values of U(VI)/Th(IV) at different temperatures confirmed the adsorption processes were spontaneous.

Key words: Acid-leached Red Mud, U(VI)/Th(IV), Adsorption, Isotherm, Kinetics

INTRODUCTION

Uranium is a radioactive element that occurs naturally in low concentrations in soil, rock, surface water and groundwater [1]. It is produced as a fuel for civil nuclear power generation. The uranium enters environment with drainage water of uranium mining and processing facilities. After the uranium has been extracted, mill tailings contain a small amount of uranium, as well as other naturally radioactive and/or toxic waste products such as thorium and radium in low concentrations. Uranium mill tailings can adversely affect public health. If not properly disposed of, the leaching and erosion of mill tailings waste not only can cause contamination of groundwater but also can pollute the nearby rivers and lakes [2].

Many separation and pre-concentration techniques such as chemical precipitation, chemical oxidation or reduction, ion-exchange, solvent extraction, reverse osmosis, electro-dialysis and adsorption on the solid have been developed to remove metal ions from waste solutions [3-10]. Adsorption has an edge over the other methods due to its free sludge, clean operation and almost complete removal of heavy metals when it is applied to very dilute effluents [11,12]. However, the adsorbent cost can be a significant fraction of the overall process costs. As such, for quite some time, efforts have therefore been made to look for cheap alternative adsorbent. The materials for this purpose include both natural materials and industrial wastes/byproducts. The adsorption of uranium(VI) and thorium(IV) by zeo-lite isolated from Metaxades (Greece), using batch type method, was studied by Misaelides et al. [13]. The biomass of *Rhizopus arrhizus* at pH 4 exhibited the highest uranium and thorium biosorptive uptake capacity in excess of 180 mg/g [14].

Red mud is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina. For every ton of alumina produced, approximately one to two tons (dry weight) of bauxite residues are generated. The very large quantity of highly caustic red mud poses very serious and alarming environmental concerns. Red mud includes valuable metallic contents and alkalinity. Considerable research has been done on the utilization of red mud as a raw material for production of a range of products such as coagulant, adsorbent, cement, ceramics, clay material, and fired building material [15]. Yet there is no economically viable and environmentally acceptable solution for the utilization of red mud.

This study relates to a process of transformation of red mud by acid leaching into a concentrated liquid or solid but soluble product, containing high amounts of Al and Fe usable as raw material for production of coagulant for water/wastewater treatment. So acid leaching of red mud will not only lead to the synchronous recovery of iron, more aluminum, titanium and others but also reduce the alkalinity of red mud. At the end of acid leaching, the acid-leached red mud will be a second by-product and it will have bigger surface area and less impurities usable as adsorbent. Our aim was to determine the effect of the basic parameters such as solution pH, contact time, dose and initial uranium/thorium concentration on the uranium/thorium adsorption by acid-leached red mud in a batch system. Thermodynamic parameters such as free energy (ΔG^o), enthalpy

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of adsorption (ΔH^o) and entropy (ΔS^o) were calculated. The applications of the isotherm models and kinetics models have been studied to explain the adsorption characteristics of the acid-leached red mud.

MATERIALS AND METHODS

The red mud was obtained from Chiping Aluminum Co. LTD of Shandong Province, China. The acid-leached red mud was prepared through acid leaching at first. It was extensively washed with distilled water and dried below 100 °C for 24 h. Dried acid-leached red mud was ground in a laboratory blender and sorted through 80 mesh sieve to maintain a uniform particle size. Th(IV) was supplied as $Th(NO_3)_4 \cdot 5H_2O$. A stock solution of U(VI) was prepared by dissolving an accurately weighted amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in distilled water. All chemicals were analytical grade too. Each experiment was performed twice at least under identical conditions.

Fourier transform infrared spectroscopy (NICOLET 380) was used to identify the chemical functional groups present on acid-leached red mud. IR spectrograms of acid-leached red mud embedded in KBr pellets were recorded for wave-numbers in the range of 400-4,000 cm^{-1}. The broad and strong peak at 3,404 cm^{-1} shows the O-H stretching vibration in aluminol (Al-OH) and silanol (Si-OH) formed on the edge surface of acid-leached red mud, while the peak observed at 1,640 cm^{-1} represents the Si-O-Si vibration. Powder X-ray diffraction (XRD) data were collected on a Phillips X'Pert Pro X-ray diffractometer with Cu K Radiation (λ=1.5405 Å). The XRD data indicate that red mud contains residual minerals from bauxite such as hematite, quartz, boehmite, gibbsite and goethite. Al_2O_3 was analyzed with the titrimetric method and SiO_2 was analyzed with the gravimetric method. Fe_2O_3 was determined by an atomic absorption spectrophotometric method. The main chemical composition of acid-leached red mud is as follows: 67.39% SiO_2, 13.86% Al_2O_3, 8.14% Fe_2O_3. The acid-leached red mud is characterized by its high percentage of SiO_2. When pH>2, the surface of SiO_2 have negative charge and metal-surface complex may be formed [16]. The visual spectrophotometer (721E) was used to determine the concentration of U(VI)/Th(IV) at 668 nm wavelength for uranium(VI) and 650 nm wavelength for thorium(IV) using U(VI)/Th(IV)-arsenazo III complex, respectively.

Batch static method was performed to optimize the basic experimental conditions for quantitative analyte adsorption such as pH dependence, adsorption isotherm and kinetic studies. Adsorption capacity of acid-leached red mud was carried out by agitating acid-leached red mud with aqueous solution of uranium/thorium of desired concentration, temperature, pH, and dose in different polyethylene plastic centrifuge tubes on shaking thermostat for predetermined time intervals, followed by centrifugation to separate acid-leached red mud from uranium/thorium solutions. Residual concentrations in the supernatant uranium/thorium solutions were determined by spectrophotometry UV-Vis. The initial pH values of the solution were adjusted by adding negligible volumes of 0.01 mol/L HNO_3 or NaOH. The adsorptive percent of U(VI)/Th(IV) (%) was calculated as

$$\text{Adsorptive percent} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

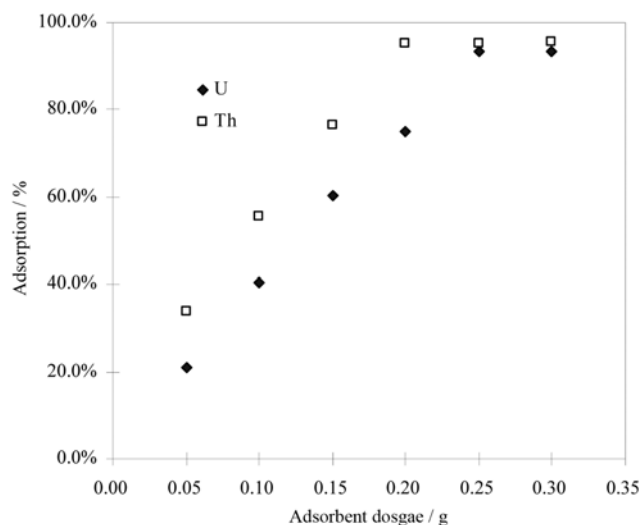where C_o is the initial concentration of U(VI)/Th(IV) solution (mg/

Fig. 1. The effect of adsorbent dosage on adsorption.

L), C_t the solution concentration at any time t (mg/L).

U(VI)/Th(IV) adsorption on acid-leached red mud was calculated by Eq. (2).

$$Q_t = \frac{(C_o - C_t)V}{W} \qquad (2)$$

where Q_t is the adsorption at any time t (mg/g), V is the volume of the solution (L), W is the mass of dry acid-leached red mud used (g).

RESULTS AND DISCUSSION

1. Adsorption Study
1-1. Effect of Adsorbent Dosage

As shown in Fig. 1, the adsorption of U(VI)/Th(IV) increased as adsorbent dosage increased from 0.05 g/L to 0.20 g/L. It may be explained that at lower acid-leached red mud dosage, U(VI)/Th(IV) were competing for limiting adsorption sites. However, as per unit mass of acid-leached red mud was increased, the more available vacant adsorption sites eased, resulting in greater adsorption of U(VI)/Th(IV). Any further addition of the acid-leached red mud beyond 0.20 g/L did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of the acid-leached red mud particles [17].

At the same dosage, the adsorption of thorium ion is more favorable than uranyl ion on acid-leached red mud. These observations can be explained in terms of three reasons. First, ions with lower hydration energy prefer the acid-leached red mud phase. Thorium has lower hydration energy (3,332 kJ/mol) than uranium (3,958 kJ/mol). This means thorium can adsorb easily on the acid-leached red mud surface. Second, thorium (1.30) is more electropositive than uranium (1.38) [18]. It explains that quadrivalent Th^{4+} adsorbed onto the negative surface should be stronger and higher than divalent UO_2^{2+}. Finally, uranium in particular is very mobile and soluble under oxidizing conditions, whereas thorium is rather immobile and insoluble under similar conditions [19].

1-2. Effect of Temperature

As can be seen from Fig. 2, like most adsorption, the extent of
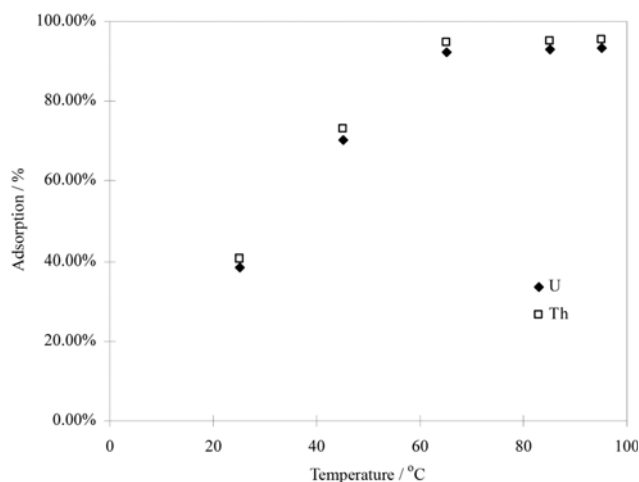
Fig. 2. The effect of temperature on adsorption.
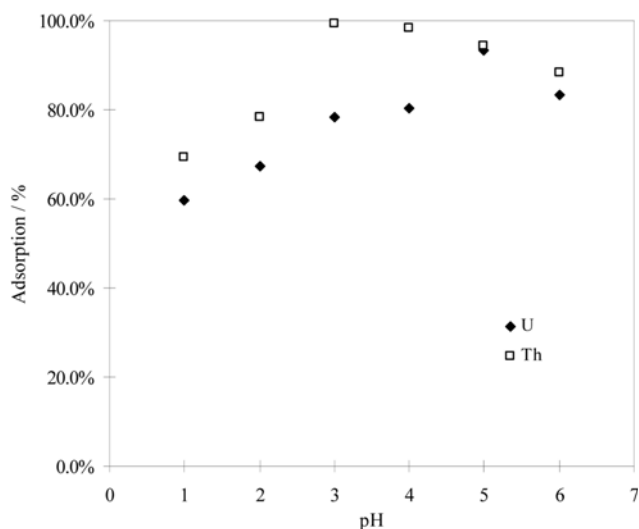

Fig. 3. The effect of solution pH on adsorption.

adsorption increases in temperature up to 80 °C and then after that it remains constant. Adsorption is an exothermic process and does not occur at lower temperature due to high kinetic energy barrier. At the same temperature, there is little difference from adsorption between uranium and thorium.

1-3. Effect of Solution pH

The solution pH is an important parameter for heavy metal adsorption. As seen from Fig. 3 the adsorption of uranium on acid-leached red mud increased with pH up to 3 and then declined with further increase in pH. The adsorption of thorium on acid-leached red mud increased with pH up to 5. At the same solution pH the acid-leached red mud is more effective for thorium than uranium.

The influence of pH on U(VI)/Th(IV) removal may be explained by H^+ competition with uranium/thorium binding sites at lower pH and the formation of extractable U(VI)/Th(IV) species at higher pH. At lower pH the surface of acid-leached red mud exhibits position sites, resulting in the reduced uptake of uranium/thorium. On the contrary, according to Collins and Stotzky [20] the hydrolyzed species can obviously be adsorbed better than the free hydrated ions. At pH values above 3, three major hydrolyzed uranium complex
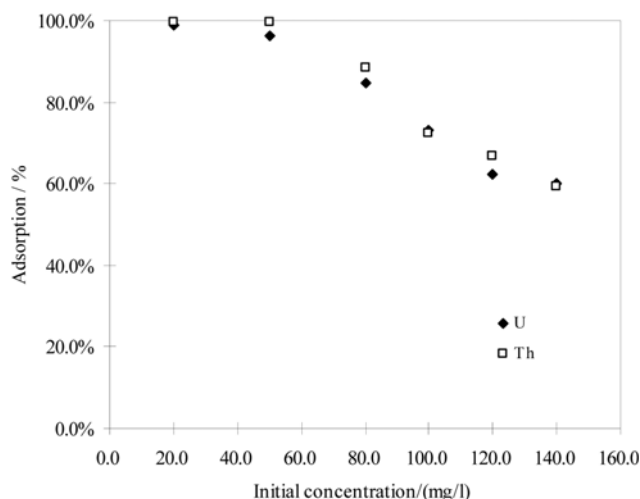

Fig. 4. The effect of initial concentration on adsorption.

ions, $(UO_2)_2(OH)_2^{2+}$, UO_2OH^+, $(UO_2)_3(OH)^{5+}$ and a dissolved solid $4UO_3 \cdot H_2O$ [21], exist in the solution. At pH values above 5, two major hydrolyzed thorium complex ions include $Th(OH)^{3+}$, $Th(OH)_2^{2+}$ and a dissolved solid $Th(OH)_4$.

1-4. Effect of Initial Concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of U(VI)/Th(IV) between the aqueous and solid phases. Hence, a higher initial concentration of uranium/thorium will enhance the adsorption process. Such an effect is clearly demonstrated in Fig. 4; at low initial U(VI)/Th(IV) concentration, the equilibrium adsorption of the acid-leached red mud is directly proportional to the initial U(VI)/Th(IV) concentration in the solution, and in the high initial U(VI)/Th(IV) concentration range, the equilibrium adsorption capacity of the acid-leached red mud go to a constant value. At the same initial concentration, the red mud has higher adsorption for thorium in comparison with uranium.

The effect of initial U(VI)/Th(IV) concentration in the range of 20 to 140 mg/L on adsorption is shown in Fig. 4. It is seen that the adsorption of U(VI)/Th(IV) was dependent on the concentration of U(VI)/Th(IV) as the decrease in the initial concentration increased the amount of U(VI)/Th(IV) adsorbed. While U(VI)/Th(IV) adsorption was found to be 98.21%/99.70% for 20 mg/L of initial U(VI)/Th(IV) concentration, this value was 60.18%/59.22% for that of 140 mg/L respectively.

1-5. Effect of Contact Time

From Fig. 5, the plot reveals that the rate of uranium/thorium adsorption is higher at the beginning. This is probably due to larger surface area of the acid-leached red mud being available at the beginning for the adsorption of U(VI)/Th(IV). Most of the maximum percent U(VI)/Th(IV) adsorption was attained after about 10 mins of contact time. The increasing contact time increased the U(VI)/Th(IV) adsorption and it remained constant after equilibrium was reached in 15 mins. The rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes, ensuring efficiency and economy.

2. Adsorption Isotherm

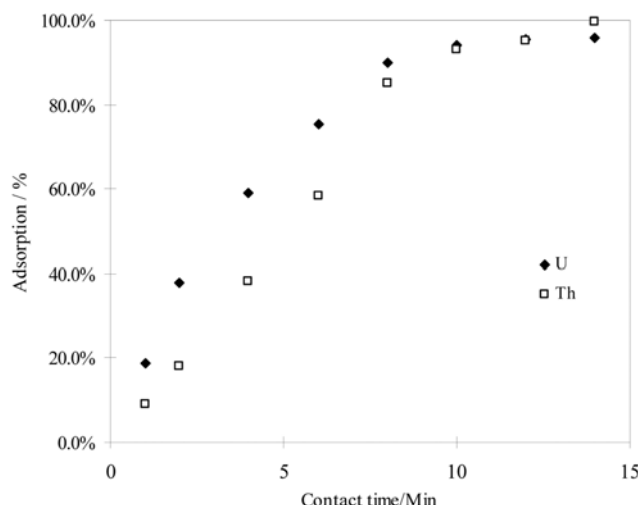Adsorption isotherms are mathematical models that describe the

Fig. 5. The effect of contact time on adsorption.

distribution of the adsorbate species between adsorbate and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich isotherms. The latter is based on the relationship between the amounts of heavy metal adsorbed per unit mass of adsorbent and the concentration of heavy metal at equilibrium. The logarithmic form of the Freundlich isotherm equation becomes,

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where n and K_F are the Freundlich adsorption constants which relate adsorption intensity and adsorption capacity.

The Langmuir isotherm is given by:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_L} + \frac{1}{Q_L K_L} \tag{4}$$

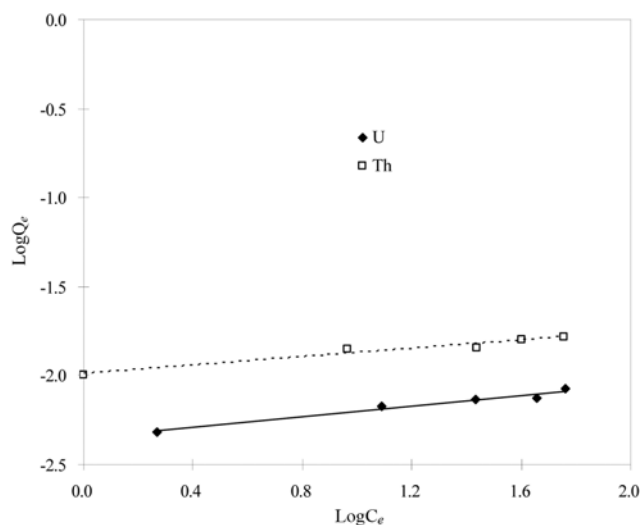where Q_L the maximum adsorption capacity (mg/mg), and K_L is

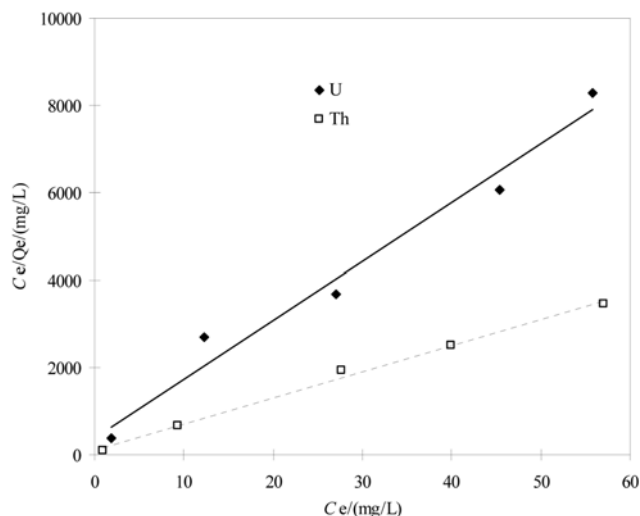**Fig. 6. Linearized Freundlich adsorption isotherms of U(VI)/Th(IV).**

Fig. 7. Linearized Langmuir adsorption isotherms of U(VI)/Th(IV).

Table 1. Isotherm parameters for U(VI)/Th(IV) adsorption by acid leached red mud

Metal ions	Freundlich isotherm			Langmuir isotherm		
	K_F	1/n	R^2	Q_L (mg/mg)	K_L	R^2
U	0.0056	0.1496	0.9664	0.0074	0.3425	0.9752
Th	0.0113	0.1238	0.9645	0.0167	0.5236	0.9959

the Langmuir binding constant which is related to the energy of adsorption (L/mg).

The linearized Freundlich and Langmuir adsorption isotherms are given in Figs. 6 and 7, respectively, whereas the isotherm parameters with the correlation coefficients are presented in Table 1. The Langmuir isotherm model best fitted with the equilibrium data since it presents higher correlation coefficient values. It indicated that the adsorption mechanism for U(VI)/Th(IV) onto acid-leached red mud may be controlled by monolayer adsorption. Due to the hydration and hydrolysis behavior, thorium has a stronger binding strength (K_L, 0.5236) at the acid-leached red mud than uranium (K_L, 0.3425).

3. Adsorption Kinetic

To analyze the kinetic mechanism of adsorption processes further, pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of U(VI)/Th(IV) adsorption onto the acid-leached red mud. The pseudo- first-order equation is given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \tag{5}$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant.

The pseudo-second-order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e}t \tag{6}$$

where k_2 (mg mg^{-1} min^{-1}) is the adsorption rate constant of pseudo-second-order.

$$h = k_2 Q_e^2 \tag{7}$$

where h (mg g^{-1} min^{-1}) is initial speed of adsorption rate as $t \rightarrow 0$
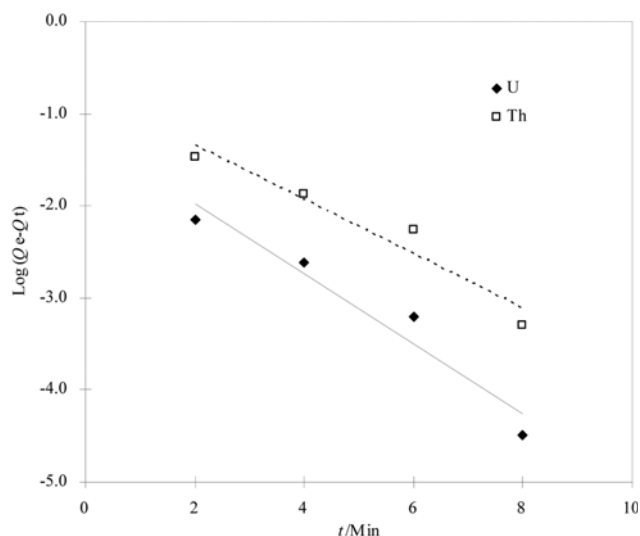
Fig. 8. Linearized Pseudo-first-order kinetic model for adsorption of U(VI)/Th(IV).
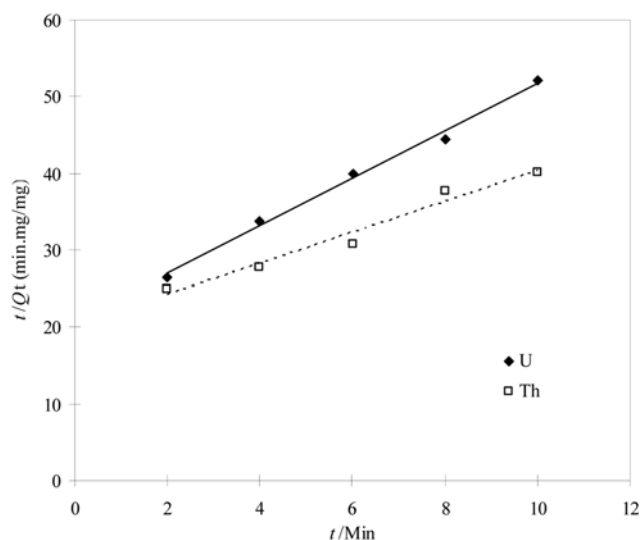

Fig. 9. Linearized Pseudo-second-order kinetic model for adsorption of U(VI)/Th(IV).

and k_2 is the rate constant of adsorption.

The linearized pseudo-first-order and pseudo-second-order kinetic models are presented in Figs. 8 and 9, respectively, whereas the kinetic parameters for adsorption of U(VI)/Th(IV) by acid-leached red mud are given in Table 2. Based on the obtained correlation coefficients, adsorption of U(VI)/Th(IV) on acid-leached red mud perfectly fit the pseudo-second-order model compared with pseudo-first-order model. The adsorption of U(VI)/Th(IV) by acid-leached red mud follows the pseudo-second-order kinetic model, which relies on the assumption that chemical adsorption may be the rate-limiting step. In addition, theoretical values of Q_e agree very much with the experimental ones Q_L, suggesting the main adsorption mechanism of chemical adsorption [22-24]. Thorium has larger ionic radius (1.19 Å) than uranium (0.91 Å), which this means uranium (k_2, 18.46) can adsorb more quickly than thorium (k_2, 7.97) at the acid-leached red mud surface.

4. Thermodynamic Study

Thermodynamic behavior of the adsorption of U(VI)/Th(IV) ions on acid-leached red mud was evaluated by the thermodynamic parameters including the change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). These parameters were calculated from the fol-

lowing equations:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \tag{8}$$

$$\Delta G^o = -RT\ln K_d = \Delta H^o - T\Delta S^o \tag{9}$$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{10}$$

where K_d is distribution coefficient, ΔH^o kJ mol^{-1} and ΔS^o J mol^{-1} K^{-1} are enthalpy and entropy changes, respectively, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T(K) is the absolute temperature. The values of ΔG^o, ΔH^o and ΔS^o were calculated by means of Eqs. (3)-(5) and shown in Table 3.

It has been reported that ΔG^o values up to -20 kJ/mol are consistent with electrostatic interaction between adsorption sites and the metal ion (physical adsorption), while ΔG^o values more negative than -40 kJ/mol involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond (chemical adsorption) [25,26]. In chemical adsorption, the metal ions stick to the adsorbent surface by forming a chemical bond and tend to find sites that maximize their coordination number with the surface.

Table 2. Kinetic parameters for U(VI)/Th(IV) adsorption by acid leached red mud

Metal ions	Pseudo-first-order			Pseudo-second-order			
	k_1 (min^{-1})	Q_e (mg/mg)	R^2	Q_e (mg/mg)	k_2 (mg min^{-1} mg^{-1})	h (mg min^{-1} mg^{-1})	R^2
U	20.19	0.023	0.8545	0.0082	18.46	1.18×10^{-3}	0.9902
Th	11.61	0.014	0.9687	0.0124	7.97	1.22×10^{-3}	0.9965

Table 3. Thermodynamic parameters for U(VI)/Th(IV) adsorption by acid leached red mud

Metal ions	ΔG^o (kJ·mol^{-1})			ΔH^o (kJ·mol^{-1})	ΔS^o (J·mol^{-1}·K^{-1})	R^2
	298 K	318 K	338 K			
U	-136.87	-140.39	-144.27	-75.68	202.55	0.9582
Th	-84.75	-87.16	-89.57	-48.46	120.41	0.9837

The negative ΔG^o values indicated the thermodynamically feasible and spontaneous nature of adsorption. However, the negative value of ΔG^o decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of U(VI)/Th(IV) is inversely proportional to temperature and removal of U(VI)/Th(IV) ions on acid-leached red mud becomes better at higher temperature, because U(VI)/Th(IV) ions are more readily desolvated. The negative values of ΔH^o suggest the exothermic nature of the adsorption of U(VI)/Th(IV) on acid-leached red mud. The positive value of ΔS^o reveals the increased randomness at the solid-solution interface during the fixation of the uranium/thorium ion on the active site of the adsorbent [27,28].

CONCLUSIONS

The present investigation shows that acid-leached red mud is an effective adsorbent for the removal of U(VI)/Th(IV) ions from aqueous solutions. Thorium(IV) is more favorable than uranium(VI) metal ions on acid-leached red mud at the same pH and initial concentration. From the kinetic studies, it is observed that adsorption of U(VI)/Th(IV) ions is very rapid in the initial stage and decreases while approaching equilibrium. The percentage removal of U(VI)/Th(IV) ions increases with the increase in adsorbent dosage and decreases with increase in initial U(VI)/Th(IV) ions concentration. Experimental results are in good agreement with Langmuir adsorption isotherm model. Adsorption of U(VI)/Th(IV) ions obeys pseudo-second order equation with good correlation.

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