

Study of the behaviour of thorium adsorption on PAN/zeolite composite adsorbent

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Abstract

The adsorption behaviour of thorium from aqueous solutions by a composite adsorbent has been investigated by a batch technique. The thorium adsorption on composite adsorbent was studied as a function of initial concentration, pH, shaking time and temperature. The sorption of thorium at the determined optimum conditions follows Langmuir, Freundlich and D–R type isotherms. Langmuir constants $Q=0.04 \text{ mmol g}^{-1}$ and $b=64.94 \text{ L mol}^{-1}$ and of D–R parameter $X_m=0.04$, $\beta=0.79$ and of sorption energy $E=0.80$ and Freundlich constants $1/n=3.12$ and $c_m=0.012 \text{ mmol g}^{-1}$ were evaluated. Thermodynamic parameters such as ΔH and ΔS were found to be $37.32 \text{ kJ mol}^{-1}$ and $206.17 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

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1. Introduction

The long-lived radionuclides in radioactive waste have been considered to be dangerous pollutants, and their migration with groundwater is strongly affected by adsorption on the geologic materials. The presence of radionuclides and toxic metals in wastes is a major environmental concern. Such wastes arise from technologies producing nuclear fuels, and from laboratories working with radioactive materials [1].

Thorium is a naturally occurring radioactive element widely distributed over the earth's crust. Some human activities such as exploitation of ores with associated thorium and nuclear fuel reprocessing can also concentrate this element [2]. Thorium is an important model element for tetravalent actinides in natural waters. It is also useful as a tracer when studying environmentally important processes [3]. 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. Solid and liquid wastes are also

produced during nuclear fuel production. Direct toxicity of thorium is low due to its stability at ambient temperatures; however thorium fine powder is self-ignitable to thorium oxide [4].

Among the discernible factors influencing the migration of thorium in natural environments, adsorption is one of the more important. Composite adsorbents/ion exchangers have been widely studied for treatment of liquid radioactive wastes. The composite ion exchangers present improved qualities with respect to those of pure inorganic exchangers or resins, such as; better selectivity for the capture of some ions, increased mechanical and chemical resistance, more regular form of the grains, smaller solubility in water than the respective inorganic compound, and better kinetics of exchange relatively to the pure inorganic exchangers. The composite ion exchangers are generally obtained by implantation of inorganic (e.g. clay minerals, cement, silica-gel or alumina) into the wide range organic materials during the polymerisation process [5,6].

The composite ion exchangers have been used in several studies to treatment of low and medium level liquid radioactive wastes [5–12], to investigate of sorption behavior of I–V group elements (Fr, Ra, Pb, Bi, Eu, Zr, Hf, Th, Nb, Pa and U) [13], to purificate of ^{223}Fr from its decay products [14], to removal of some basic dyes [15], and Na from irradiated samples [16] and to mineralize of biological materials in neutron activation analysis [17].

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This paper deals with the investigation of the best separation and recovery conditions of thorium on a PAN/zeolite composite adsorbent as a function of the initial thorium concentration, pH, shaking time and temperature.

2. Experimental

2.1. Materials and methods

The zeolite (clinoptilolite) from Manisa-Gordes, Turkey was obtained from Pamukkale University, Turkey. The clinoptilolite was ground and wet sieved to a particle size of -200 mesh. Polyacrylonitrile (PAN) fiber was obtained from the Industry of Acrylic Chemistry (AKSA), Istanbul, Turkey.

The composite adsorbent has been prepared from inorganic adsorbent, a natural zeolite clinoptilolite, as an active component and polyacrylonitrile (PAN) as a binding polymer. The composite beads were prepared in a flask with reflux as a reactor. Very fine colloidal particles of the clinoptilolite (-200 mesh) were stirred with the solution of PAN which was solved in 11.86 g of *n*-dimethylformamide (DMF) at 70°C for 1 h to form homogeneous solution. The mass ratio of the PAN to the clinoptilolite was adjusted at 1:1 [18]. The mixture was fed into the nozzle to obtain the spherical composite beads. Ultra pure distilled water (Millipore) was used as a gelation agent. The composite beads were washed repeatedly by ultra pure distilled water to remove the solvent and then dried at 60°C . Obtained the spherical composite beads were sieved and fractionated according to the particle size. The dried composite adsorbent was stored in wide mouth plastic bottle for further use. It was assumed that the composite beads have homogeneous distribution of the inorganic particles in their matrix structure.

Arsenazo III and $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were obtained from Merck Co. All chemicals used were of analytical reagent grade and all solutions were prepared with pure distilled water. One thousand microlitres per millilitre of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ solution was prepared and used for adsorption experiments. The buffer solutions (pH 4, 7 and 9) to calibrate the pH-meter model 8521 from Hanna Instruments were purchased from Merck. In all experiments, ultra pure distilled water was used for analytical purposes.

2.2. Adsorption experiments

The sorption experiments have been studied by a batch technique. The batch technique was carried out in a thermostatted shaker bath GFL-1083 model. The shaking rate was the same for all the experiments. The prepared composite adsorbent (0.03 g) and standard $\text{Th}(\text{NO}_3)_4$ (10 mL) aqueous solution were shaken at different temperature for various mixing time. Filter-separating of solid phase from liquid was followed by centrifuging at 300 rpm for 10 min. The thorium was determined spectrophotometrically using Arsenazo III method as complexing agent at 665 nm against reagent blank, employing Shimadzu UV-vis 260 Spectrophotometer [19]. For calculating the thorium concentration, the sorption of solution was compared with a working curve that was a plot of absorbance versus standard concentration of thorium. The amount of adsorbed thorium was estimated

from the difference of the thorium concentrations in the aqueous before and after the adsorption because adsorption of Th(IV) onto the wall of polyethylene test tubes was found to be negligible under the experimental conditions used. All experiments were carried out at 298 K. The experiments were carried out in duplicate. Standard deviation never exceeded 5% for each replicate.

Distribution coefficients K_d are defined as the ratio of the concentration of the thorium in the sorbent and in the solution at equilibrium. The distribution coefficients and adsorption yield (%) were calculated by using the following expression:

$$K_d = \left[\frac{C_i - C_e}{C_e} \right] \frac{V}{m} \text{ (mL/g)} \quad (1)$$

$$\text{adsorption yield (\%)} = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \quad (2)$$

where C_i is the concentration of the initial solution, C_e the concentration of the solution in equilibration, V the volume of the solution (mL) and m is the grams of the composite adsorbent.

2.3. Desorption experiments

Desorption of thorium was performed also by batch technique. Some desorptive reagents were treated with loaded adsorbent to recover thorium from the adsorbent as a function of desorptive reagents concentration, time and temperature.

2.4. Adsorption isotherm

The adsorption isotherms were obtained by analyzing solutions in contact with composite adsorbent before and after equilibrium and plotted in terms of the equivalent fraction of thorium in the composite phase against the equivalent fraction in the solution phase.

2.5. Thermodynamic parameters

A 0.03 g of composite adsorbent was treated with thorium solution in different temperatures. The thermodynamic parameters (ΔH , ΔG and ΔS) were calculated from the sorption data.

3. Results and discussion

3.1. Adsorption experiments

The effects of various parameters such as initial thorium concentration, pH, contact time and temperature were investigated.

3.1.1. Effect of initial concentration

One of the most important parameters on the sorption system, which can influence the sorption behavior of thorium, is the initial thorium concentration. Fig. 1 shows the distribution coefficients for Th(IV) on the composite adsorbent as a function of the initial uranium concentration in the range of $10\text{--}300 \mu\text{g mL}^{-1}$ at 30°C . The sorption yield of 100% in the range of $10\text{--}100 \mu\text{g mL}^{-1}$ was obtained. After the concentration

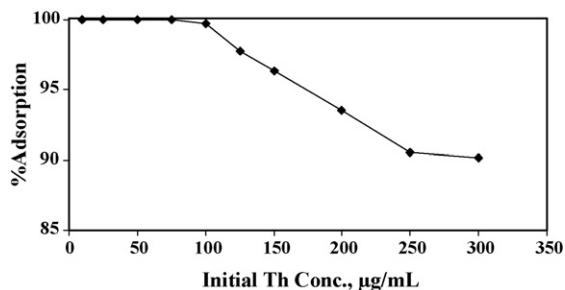


Fig. 1. Effect of initial thorium concentration.

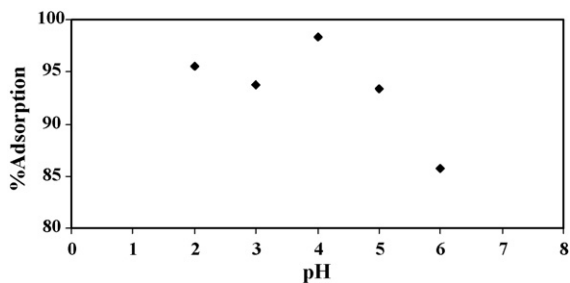


Fig. 2. Sorption yield of Th(IV) onto composite adsorbent as a function of pH.

of $100 \mu\text{g mL}^{-1}$, the sorption yield was decreased with increasing initial thorium concentration. In further experiments thorium concentration of $125 \mu\text{g mL}^{-1}$ was used.

3.1.2. Effect of pH

The effect of pH on the sorption of thorium was studied from pH 2 to 6 at 30°C . pH of thorium standard solution was adjusted with acetic acid/acetate buffer solution. Fig. 2 shows the effect of pH on thorium sorption on the adsorbent. Below pH 3, the predominant thorium ion would be the positively charged Th^{4+} . When the pH of solution is increased to pH 4, the 1:1 and 1:2 positively charged thorium acetate complexes $[\text{ThCH}_3\text{COO}]^{3+}$ and $[\text{Th}(\text{CH}_3\text{COO})_2]^{2+}$ are characteristic ions. Thorium sorption yield on the composite adsorbent reached a maximum of 97.75% at pH 4. Above pH 4, the sorption yield decreases with increasing pH.

3.1.3. Effect of shaking time

The sorption of Th(IV) ions has been investigated onto the composite adsorbent as a function of shaking time in the range of 5–300 min. The results are given in Fig. 3. As seen from Fig. 3,

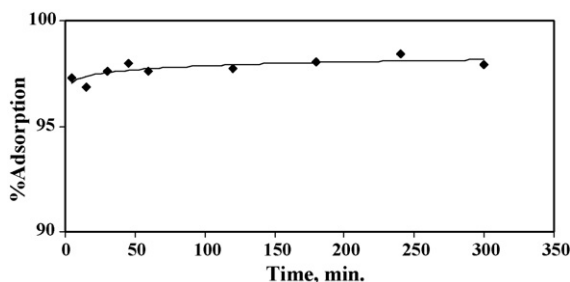


Fig. 3. Effect of shaking time on sorption of Th(IV) ions onto composite adsorbent.

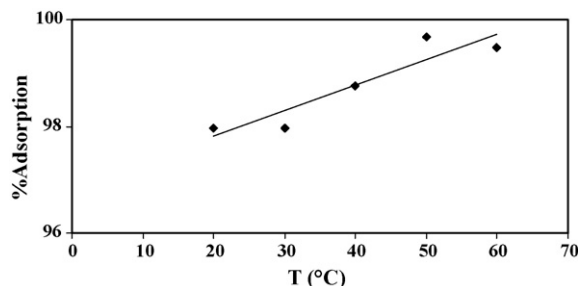


Fig. 4. Dependence of sorption of Th(IV) onto composite adsorbent on temperature.

the sorption yield slightly increases with increasing shaking time and attains equilibrium as 97.97% sorption within 45 min.

3.1.4. Effect of temperature

The sorption of Th(IV) ions onto the composite adsorbent was studied as a function of temperature from 20 to 60°C employing 45 min shaking time in the presence of $125 \mu\text{g mL}^{-1}$ at pH 4. Fig. 4 illustrates sorption percent as a function of the temperature. It was observed that thorium sorption yield was increased with increasing temperature.

3.2. Thermodynamic parameters

The influence of temperature variation was examined on the sorption of Th(IV) ions onto the composite adsorbent from $125 \mu\text{g mL}^{-1}$ of sorptive solution from 20 to 60°C using 45 min equilibrium time. The equations given below were used to evaluate the values of ΔH , ΔS and ΔG [20]:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

The plot of $\ln K_d$ versus $1/T$ (K^{-1}) is shown in Fig. 5. From the slope and intercept of the plot the values ΔH and ΔS and from Eq. (3) ΔG are computed to be $37.32 \text{ kJ mol}^{-1}$, $206.17 \text{ J mol}^{-1}$ and average $-27.21 \text{ kJ mol}^{-1}$, respectively. The positive values of ΔH and negative ΔG indicate endothermic and spontaneous nature of sorption, respectively (Table 1).

3.3. Sorption isotherms

The sorption data have been subjected to different sorption isotherms namely Langmuir, Freundlich and Dubinin–

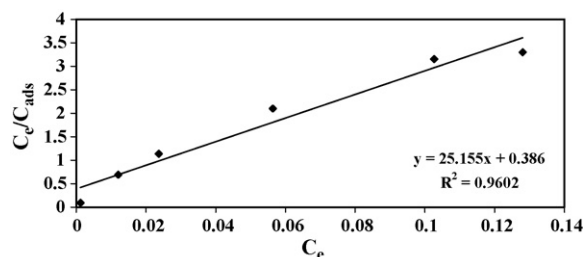


Fig. 5. Langmuir isotherm.

Table 1
Thermodynamic parameters of sorption system

ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹)	ΔG (kJ mol ⁻¹)				
		293 K	303 K	313 K	323 K	333 K
37.32	206.17	-23.09	-25.15	-27.21	-29.27	-31.33

Radushkevich (D–R). The Langmuir adsorption isotherm was tested in the following linearized form:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (4)$$

where C_e is the equilibrium concentration of Th(IV) in solution (mmol L⁻¹) and C_{ads} is the amount of Th(IV) ions sorbed onto composite adsorbent (mol g⁻¹), Q and b are Langmuir constant related to sorption capacity and sorption energy, respectively [21]. A linear plot is obtained when C_e/C_{ads} was plotted against C_e over the entire concentration range of Th(IV) ions investigated. From the slope and intercept of this plot the values of $Q=0.04$ mmol g⁻¹ and of $b=64.94$ L mol⁻¹ have been evaluated. The Langmuir model is developed to represent chemisorption on a set of well-defined localized adsorption sites having same sorption energies independent of surface coverage and no interaction between adsorbed molecules. Maximum sorption capacity (Q) represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature.

The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The numerical value of $1/n < 1$ indicates that sorption capacity is only slightly suppressed at lower equilibrium concentration. This isotherm does not predict any saturation of the sorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface [20–22]. The thorium sorption data were applied on the following linearized form of Freundlich sorption isotherm:

$$\log C_{\text{ads}} = \log C_m + \frac{1}{n} \log C_e \quad (5)$$

by plotting $\log C_{\text{ads}}$ versus $\log C_e$. The plot is shown in Fig. 6. The sorption data obeyed down to 100 $\mu\text{g mL}^{-1}$ thorium concentration very well. From the slope and intercept of linearized portion of the plot the sorption intensity ($1/n$) and capacity (C_m)

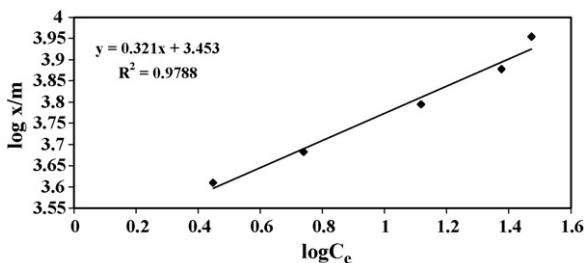


Fig. 6. Freundlich isotherm.

are computed to be $1/n=0.32$ and $C_m=0.012$ mol g⁻¹, respectively.

The sorption data have been applied to D–R model. This is postulated within an adsorption space close to sorbent surface. If the surface is heterogeneous and an approximation to a Langmuir isotherm is chosen as a local isotherm for all sites that are energetically equivalent then the quantity $\beta^{1/2}$ can be related to the mean sorption energy, E , which is the free energy of the transfer of 1 mol of thorium ions from infinity to the surface and sorbent. The difference in the free energy between the adsorbed phase and saturated liquid sorbate is referred as adsorption potential which was first put forward by Polanyi and later developed by Dubinin and his coworkers. The D–R equation was examined in following linearized form:

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2 \quad (6)$$

where X_m is the maximum sorption capacity, β the activity coefficient related to mean sorption energy and ε is the Polanyi potential which is equal to

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R is the gas constant in kJ mol⁻¹ and T is the temperature in K. The saturation limit (X_m) may represent the total specific micropore volume of the sorbent. The sorption energy can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

Fig. 7 shows the plot of $\ln C_{\text{ads}}$ versus ε^2 . From the slope and intercept of the plot the values of $\beta=0.79$ mol² J⁻² and of $X_m=0.04$ mmol g⁻¹ has been estimated. The value of E is estimated to be 0.80 J mol⁻¹.

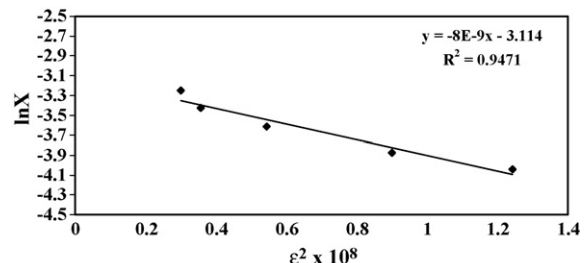


Fig. 7. D–R isotherm.

Table 2
Effect of some elution reagents for thorium desorption

Reagents	Loaded Th (μg)	Desorbed Th (μg)	% desorption
1 M HNO_3	1232.16	167.70	13.61
1 M H_2SO_4	1232.16	98.82	8.02
1 M HCl	1232.16	184.58	14.98
1 M EDTA	1232.16	114.71	9.31
Distilled water	1232.16	–	–
1 M NaOH	1232.16	–	–
1 M NaNO_3	1232.16	–	–
1 M Na_2SO_4	1232.16	–	–
1 M CH_3COONa	1232.16	–	–

–: not determined.

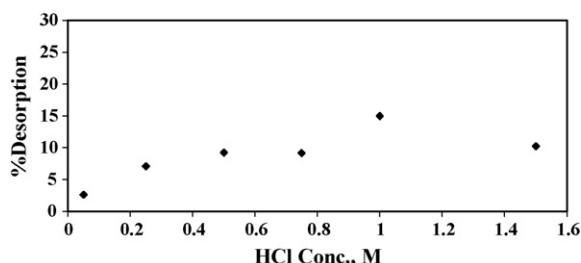


Fig. 8. Dependence of thorium desorption on HCl concentration.

3.4. Desorption experiments

Desorption of thorium was performed also by batch technique. Some desorptive reagents given in Table 2 were treated with loaded adsorbent to recover thorium from the adsorbent.

3.4.1. Effect of HCl concentration

The thorium desorption was studied as a function of HCl concentration from 0.05 M HCl solution to 1.5 M HCl solution employing 1 h shaking time at 30 °C. Fig. 8 shows the dependence of thorium desorption on HCl concentration. Maximum desorption (14.98%) is achieved from 1 M HCl solution which is selected as a desorptive medium.

3.4.2. Effect of desorption time

The thorium desorption from loaded composite adsorbent has been investigated as a function of equilibrium time in the range of 5–180 min. The results are given in Fig. 9. Desorption yield decreases slightly with increasing shaking time and attains equilibrium within 15 min corresponding to 14.45%. Therefore, in further experiments 15 min equilibrium time was used.

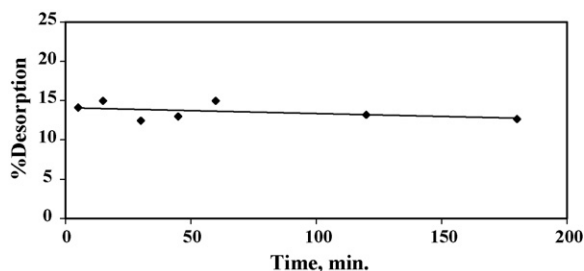


Fig. 9. Percent desorption of thorium as a function of equilibrium time.

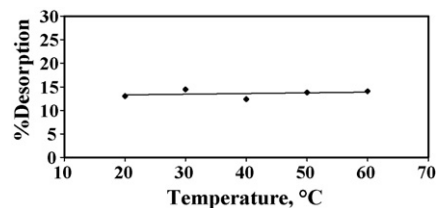


Fig. 10. Influence of temperature on desorption of thorium.

3.4.3. Effect of temperature

Effect of temperature in desorption process of thorium was investigated from 20 to 60 °C employing 15 min shaking time with 1 M HCl. Fig. 10 shows influence of temperature on the desorption of thorium from the composite adsorbent. Desorption yield was not significantly changed with increasing temperature. Desorption yield of 14.45% was reached at 30 °C.

4. Conclusions

The adsorption behavior of Th(IV) onto the composite adsorbent was investigated. It was found that PAN/zeolite composite adsorbent is economical and effective sorbent for Th(IV) ions and the composite adsorbent exhibited an excellent adsorption selectivity for Th(IV).

The sorption of Th(IV) ions onto the composite adsorbent follows Langmuir, Freundlich and D–R isotherms.

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.

Nevertheless thorium recovery is the more difficult step, owing to its great affinity towards the adsorbent. With hydrochloric acid solution, the desorption of Th(IV) is very slow and its level is very low. Desorption percent for this adsorbent was 14.48%. This may result from creating different chemical forms of thorium with some components of the composite adsorbent and this may suggest that, aside from ion exchange, some other mechanisms are involved in the observed process.

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