



Sorption of uranium(VI) from aqueous solutions by akaganeite

Sabriye (Doyurum) Yusan*, Sema Akyil

Ege University, Institute of Nuclear Sciences, 35100 Bornova-IZMIR, Turkey

ARTICLE INFO

Article history:

Received 12 November 2007

Received in revised form 4 February 2008

Accepted 3 March 2008

Available online 18 March 2008

Keywords:

Uranium(VI)

Sorption

Iron oxides

Adsorption isotherms

Thermodynamic constants

ABSTRACT

Removal of U(VI) ions from aqueous solutions was investigated using synthetic akaganeite-type nanocrystals. Nanocrystals of iron oxyhydroxides were synthesized with two different methods and then compared their adsorption capacities. Akaganeite (β -FeOOH) was synthesized in the laboratory by precipitation from aqueous solution of Fe(III) chloride and different precipitating agents. The relative importance of test parameters like solution pH, contact time, temperature and concentration of adsorbate on adsorption performance of akaganeite for U(VI) ion were studied. Typical adsorption isotherms (Langmuir, Freundlich, Dubinin-Raduskevich) were determined for the mechanism of sorption process. Also the thermodynamic constants (ΔH° , ΔS° and ΔG°) were calculated. The product materials were examined by powder X-ray diffraction for crystalline phase identification and scanning electron microscope (SEM).

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

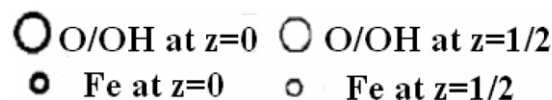
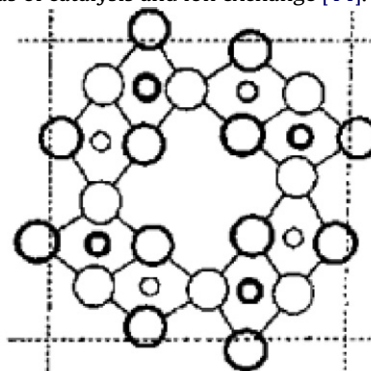
Uranium is one of the most important heavy metals because of the chemical toxicity and radioactivity. Excessive amounts of uranium have entered into environment through the activities of nuclear industry. It is usually found in the environment in the hexavalent form. The toxic nature of uranium(VI) ions, even at trace levels, has been a public health problem for many years. For this reason, removal of uranium from wastewater is of great importance [1].

Various techniques are employed for the removal of uranium ions from wastewaters and radioactive wastes. Precipitation, membrane processes, ion exchange, solvent extraction and adsorption are the most common used methods [2,3]. For adsorption of uranium(VI) from wastewater, many researchers have used various solids, which are natural, organic and inorganic; for example, coir pith [4], zeolite [1,5,6], cork biomass [7], goethite [8], activated carbon [2], and cement [9].

Metal oxides or hydroxides of iron, aluminum and manganese play a very important role in the sorption of contaminants in wastewater systems [1]. Iron oxides and oxyhydroxides are of technological importance as catalysts, sorbents, pigments, flocculents, coating, gas sensors and size-selective anion-exchange materials [10]. Iron-based adsorbents are useful due to their economic and safety merits. Iron-oxyhydroxide is known to occur commonly as goethite (α -FeOOH), akaganeite (β -FeOOH), and lepidocrocite (γ -FeOOH) [11]. These minerals have high sorption capacities for metal and anionic contaminants such as arsenic, chromium, lead, mer-

cury, selenium, phosphate and uranium [12].

Akaganeite (β -FeOOH), a natural product of the corrosion of iron in chloride-containing environments, has a tetragonal structure consisting of double chains of edgeshared octahedra that share corners with adjacent chains to form channels running parallel to the c -axis. Among the iron compounds, the iron oxyhydroxide phase akaganeite, β -type FeOOH, has a large tunnel-type structure where iron atoms are strongly bonded to framework [13]. This tunnel structure makes β -FeOOH an especially interesting material in the areas of catalysis and ion exchange [14].



The sketch of the β -FeOOH framework [13]

* Corresponding author. Tel.: +90 232 388 64 66; fax: +90 232 388 64 66.
E-mail address: sabriye.doyurum@ege.edu.tr (S. Yusan).

In this work, sorbent, akaganeite (β -FeOOH) was synthesized in the laboratory by precipitation from aqueous solutions of Fe(III) chloride and two different precipitating agent and adsorbents obtained were called as Akaganeite-1 (AK-1) and Akaganeite-2 (AK-2). This paper deals with the investigation of the best separation and recovery conditions of uranium on akaganeite adsorbent as a function of the initial uranium concentration, pH, shaking time and temperature. The thermodynamic parameters such as free energy (ΔG°), enthalpy of adsorption (ΔH°) and entropy (ΔS°) were calculated. The applications of the isotherm models have been studied to explain the adsorption characteristics of the akaganeite.

2. Experimental

2.1. Materials

Synthesis of AK-1 was like that, 0.1 M NaOH solution was slowly added to 500 mL of a 0.1 M FeCl₃ solution in a 2 L beaker at room temperature until the pH of the mixture was attained around 10. The mixture was stirred magnetically during the addition of the NaOH solution. The suspension was further stirred for 1 h. The precipitate was separated by centrifugation, washed with deionized water until neutral and finally dried in air at room temperature [11].

AK-2 was prepared by precipitation from an aqueous solution of iron(III) chloride (0.506 M with respect to Fe³⁺). For the hydrolysis process an aqueous solution of ammonium carbonate (0.002 M) was added dropwise at a constant flow rate. Vigorous mechanical stirring was applied in order to achieve good mixing and the addition of ammonium carbonate was stopped when the pH was 8.0. The reaction mixture was stirred for an additional 30 min at the adjusted reaction temperature. The reaction product was decanted in a cellulose membrane for the removal of chlorine anions and subsequently was freeze-dried in a benchscale instrument (Christ Alpha 1–4) [15].

All chemicals and reagents used for experiments and analyses were of analytical grades. A stock solution of 1000 mg L⁻¹ U(VI) was prepared by dissolving an appropriate amount of UO₂(NO₃)₂·6H₂O in deionized water. The initial pH of the working solutions was adjusted by addition of HNO₃ or Na₂CO₃. Dibenzoyl methane-tri-*n*-octyl phosphine oxide (DBM-TOPO), salicylic acid was obtained from Merck Co. The buffer solutions (pH 4, 7 and 9) to calibrate the pH-meter Model 8521 from Hanna Instruments were also purchased from Merck.

2.2. Characterization of the materials

Powder X-ray diffraction (XRD) data were collected on a SHIMADZU XDD-6000 diffractometer with Cu-X radiation ($\lambda = 1.5405 \text{ \AA}$). The data were collected at room temperature in the range of 2θ between 5° and 70°. The diffractogram of akaganeite is

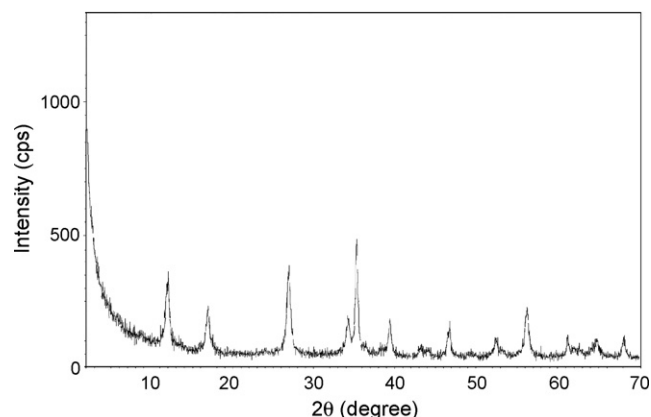


Fig. 1. XRD pattern of AK-2.

shown in Fig. 1. As shown in Fig. 1, this adsorbent has low crystallinity with d values. Similar result has been obtained in the literature [13,16].

Scanning electron microscope (SEM) images were taken on Jeol Jsm 6060 scanning electron microscope. The SEM images were shown in Fig. 2. The SEM images showed that akaganeite prepared under conventional conditions had the similar morphology. The crystallites in both products had similar cigar-like shapes and similar crystal sizes.

2.3. Batch adsorption experiment

Batch adsorption experiments were carried in a thermostated shaker bath, GFL-1083 model. AK-1 and AK-2, which have 75 μm particle size, (0.01 g) were added to 10 mL solution containing various uranium concentrations at different temperatures for various contact time. The pH was adjusted by adding HNO₃ and Na₂CO₃ to the solutions at the each experiment. The suspension was filtrated by using Whatman filter paper no: 44. A simple and sensitive spectrophotometric method was used in the experiments to determine uranium in solution. The uranium remained in solution was analyzed with the DBM-TOPO as complexing agent at 405 nm against reagent blank employing spectrophotometric method on Shimadzu UV-1601 UV-VIS spectrophotometer [17,18]. The amount of adsorbed uranium was estimated from the difference of the uranium concentrations in the aqueous phase before and after the adsorption. The influence of specific process parameters such as initial uranium concentration, pH of the solution, contact time and temperature was determined by calculating uranium(VI) sorption by akaganeite and changing a parameter and keeping other parameters constant. Each experiment was repeated three times and the results given are the average values. The percentage adsorption of

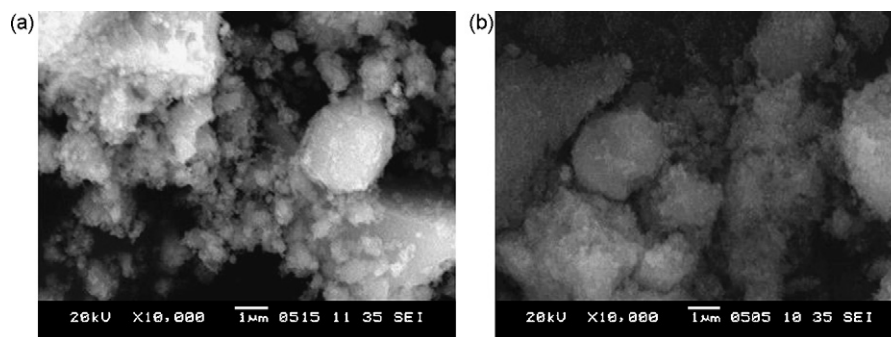


Fig. 2. SEM patterns of akaganeite (a) AK-1 ($\times 10,000$, 1 μm) (b) AK-2 ($\times 10,000$, 1 μm).

Table 1
Conditions of the leaching processes

Parameter	Uranium-acidic leachate solution
Amounts of ore	500 g
Solid/aqua ratio	2/3
Concentration of reagent	175 kg H ₂ SO ₄ /ton
Leaching time	3 h
Temperature	24 °C

uranium from aqueous solution was computed as follows:

$$\text{Adsorption \%} = \frac{C_{\text{int}} - C_{\text{fin}}}{C_{\text{int}}} 100 \quad (1)$$

where C_{int} and C_{fin} are the initial and final uranium concentration, respectively.

After obtaining the optimum adsorption conditions of the akaganeite, the uranium adsorption capacities were determined. 0.01 g of the adsorbents contacted with 10 mL of 2380 mg L⁻¹ of standard uranium solution at 30 °C for 24 h. The adsorption capacity for UO₂²⁺ was determined spectrophotometrically using salicylic acid method as complexing agent at 468 nm against reagent blank [19]. The amount of adsorbed uranium was estimated from the difference of the uranium concentrations in the aqueous solution, before and after adsorption. Each experimental result was obtained by averaging the data from three parallel experiments. According to this method, uranium adsorption capacities of AK-1 and AK-2 were calculated as 0.49 mmol g⁻¹ adsorbent and 0.38 mmol g⁻¹ adsorbent, respectively.

2.3.1. Desorption experiments

AK-1 and AK-2, which are loaded at optimum uranium adsorption conditions were used for desorption studies. Desorption of uranium was achieved using different concentrations of HCl and HNO₃. Loaded sorbents were contacted with acid solutions for various contact time at 30 °C in the thermostated shaker. The final uranium concentration in the aqueous phase was determined with a Shimadzu UV-1601 UV-VIS spectrophotometer by measuring absorbance at λ_{max} of 405 nm. The desorption ratio was calculated from the amount of uranium adsorbed on the sorbents and the final uranium concentration in the desorption medium, using the following equation

$$\text{Desorption ratio (\%)} = \frac{\text{amount of metal ion desorbed}}{\text{amount of metal ion adsorbed}} 100$$

2.4. Application of akaganeites

The uranium solution from matrix medium on the akaganeite was studied by batch technique. Acidic leach solution including uranium was used as matrix medium. The ore samples were taken from Koprubasi-Manisa district in Western Aegean Region in Turkey. It is well known that there are uranium anomalies in these districts and uranium exploration of this ore sample was accomplished by radio-metric and chemical analysis at Ege University, Institute of Nuclear Sciences [20–22]. The leaching solution was obtained under the conditions given in Table 1.

A known weight, i.e., 0.01 g of the akaganeites was equilibrated with 10 mL of leaching solutions containing uranium at a fixed temperature (30 °C) in a thermostated shaker for 2 and 1 h for AK-1 and AK-2, respectively. After equilibration, the suspension was filtered with Whatmann 40 paper. The amounts of uranium and other elements in the solutions were determined by Perkin Elmer Optima 2000 DV Inductively Coupled Plasma–Optical Emission Spectrometer (ICP–OES) on the basis of initial concentration.

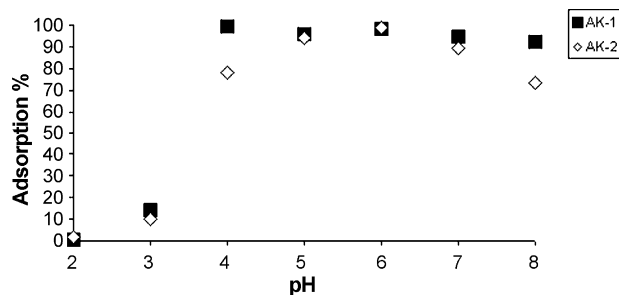


Fig. 3. The effect of pH on the uptake of U(VI) by AK-1 and AK-2 (m : 0.010 g, c : 50 mg L⁻¹, v : 10 mL, t : 2 h).

Also a synthetic matrix solution including some heavy metals was prepared and equilibrated with 10 mL of matrix solutions at a fixed temperature (30 °C) in a thermostated shaker for 2 and 1 h for AK-1 and AK-2, respectively. After equilibration, the suspension was filtered with Whatmann 44 paper. The amounts of uranium and other elements in the solutions were determined by Perkin Elmer Optima 2000 DV ICP–OES on the basis of initial concentration.

3. Results and discussion

3.1. Effect of the pH variation

The effect of pH on the adsorption capacity of akaganeite was investigated using solution of 50 mg L⁻¹ uranium(VI) for a pH range of 2.0–8.0 at 25 °C for 120 min. After sorption equilibrium, the concentration of the metal ion in the filtrate was determined by spectrophotometer. The experimental results are presented in Fig. 3, where the uranium removal is plotted against the solution pH. As shown in Fig. 3, the uranium removal by akaganeite was strongly depended on variations of the solution pH. Maximum uranium attenuation was obtained as 99.32% at pH 4.0 for AK-1 and as 99.03% at pH 6.0 for AK-2. At higher acidic conditions, uranium(VI) uptake was minimal due to increasing positive characteristic of the surface of adsorbent. Since the species to be adsorbed are also positive, the adsorption is not favored. Besides this, H⁺ ions present at higher concentration in the reaction mixture compete with positive ions for the adsorption sites resulting in the reduced uptake of uranium. On the contrary, as the pH increases the adsorbent surface becomes more negatively charged and therefore the adsorption of positively charged species is more favorable. As pH increased from 2.0 to 6.0, the amount of U(VI) adsorbed on akaganeite increased with pH. At pH values higher than 9.0, uranium(VI) occurs in the solution only in the form of carbonate-complex ions that are highly negative charged. So they could competed to bound the adsorption sites with uranium(VI) and beside this occupation of adsorption sites with uranium(VI) ions is decreased as concentration of dissolved carbonate and bicarbonate anions increased [1].

3.2. Effect of uranium concentration

To study sorption equilibrium, uranium(VI) solutions containing 50–250 mg U L⁻¹ were kept in contact with akaganeite for 2 h at pH 4.0 for AK-1 and at pH 6.0 for AK-2 while keeping all other parameter constant. The results are shown in Fig. 4. The percentage adsorption of U(VI) decreases with increasing uranium concentration in the aqueous solution. In the diluted solutions, the mobility of uranyl ions (UO₂)²⁺ is high. For this reason probably the interaction of this ion with the adsorbent was increased.

3.3. Effect of contact time

The adsorption experiments were carried out for contact times ranging from 15 to 360 min with fixed amounts of adsorbent (0.01 g)

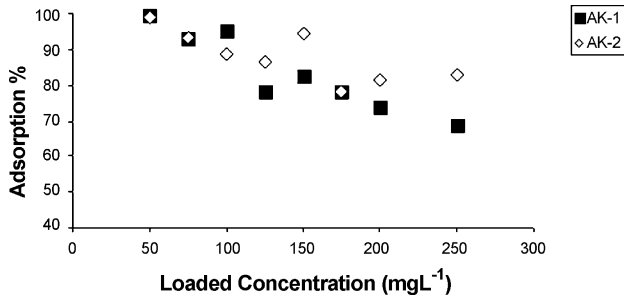


Fig. 4. The effect of concentration on the uptake of U(VI) by AK-1 and AK-2. (for AK-1; c: 50 mg L⁻¹, v: 10 mL, t: 2 h, pH 4.0, m: 0.010 g; for AK-2, c: 50 mg L⁻¹, v: 10 mL, t: 2 h, pH 6.0, m: 0.010 g).

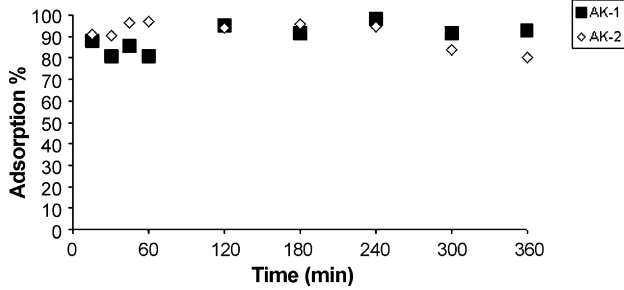


Fig. 5. The effect of contact time on the uptake of U(VI) by AK-1 and AK-2. (for AK-1; c: 100 mg L⁻¹, v: 10 mL, pH 4.0, m: 0.010 g, for AK-2; c: 150 mg L⁻¹, v: 10 mL, pH 6.0, m: 0.010 g).

at ambient temperature (25 °C) while keeping all other parameters constant. Fig. 5 shows the variations of percentage adsorption with contact time for U(VI) at pH 4.0 and pH 6.0 for AK-1 and AK-2, respectively. According to obtained data, the highest value of adsorbed U(VI) ion on the AK-1 was reached 95.09% for 120 min and 96.72% for 60 min for AK-2. The uranium adsorption is fast and attains equilibrium in about 60 min after mixing.

3.4. Effect of temperature

The temperature dependent data were obtained by varying temperature from 25 to 50 °C while the other parameters were kept constant. Fig. 6 shows the effect of temperature on the batch adsorption of U(VI). It was observed that the uptake of uranium for AK-1 was slightly increased with increasing temperature from 25 to 50 °C. However, the rise in temperature caused to slightly decrease the percentage removal of U(VI) for AK-2.

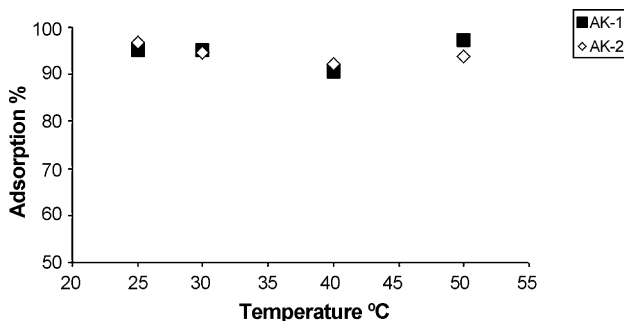


Fig. 6. The effect of temperature on the uptake of U(VI) by AK-1 and AK-2. (for AK-1; c: 100 mg L⁻¹, v: 10 mL, pH 4.0, t: 120 min, m: 0.010 g, for AK-2; c: 150 mg L⁻¹, v: 10 mL, pH 6.0, t: 60 min, m: 0.010 g).

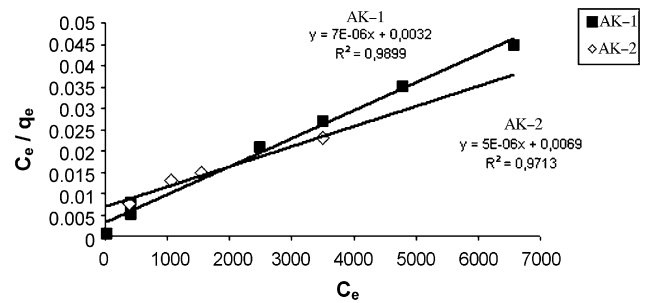


Fig. 7. Langmuir isotherm for AK-1 and AK-2.

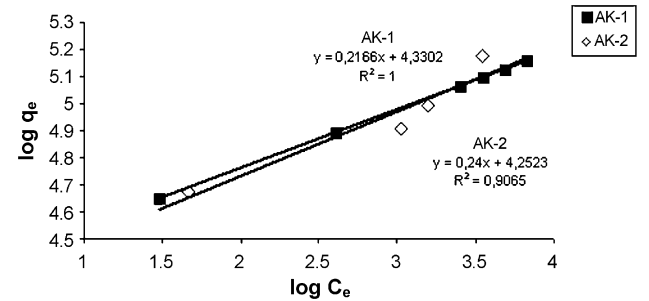


Fig. 8. Freundlich isotherm for AK-1 and AK-2.

3.5. Sorption isotherms

The sorption data have been subjected to different sorption isotherms, namely Langmuir, Freundlich and Dubinin-Radushkevich (D-R). These isotherm equations are commonly used for describing adsorption equilibrium for water and wastewater treatment applications. The adsorption isotherms thus obtained are depicted in Figs. 7–9.

The sorption data for U(VI) in the concentration range used was fitted using Langmuir equation. The values of b and Q° were calculated from Eq. (2). According to Langmuir model, adsorption occurs uniformly on the active sites of the sorbent and once a sorbate occupies a site, no further sorption can take place at this site. The Langmuir equation has the form:

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \quad (2)$$

where q_e is the amount adsorbed at equilibrium (mg g⁻¹), C_e is the equilibrium concentration (mg L⁻¹), b is a constant of the sorption equilibrium (L mg⁻¹), and Q° is the saturated monolayer sorption capacity (mg g⁻¹) [2,4].

By plotting C_e/q_e versus C_e , Q° and b can be determined if a straight line is obtained. The Langmuir adsorption isotherms are given in Fig. 7.

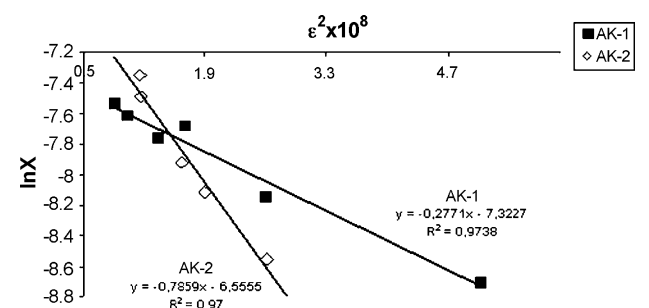


Fig. 9. D-R isotherm for AK-1 and AK-2.

Table 2
Values of Langmuir, Freundlich and Dubinin-Radushkeviche (D-R) constants

Adsorbents	Langmuir model			Freundlich model			D-R model		
	R^2	Q° (mmol g ⁻¹)	b (g L ⁻¹)	R^2	K_F (mmol g ⁻¹)	n	R^2	X_m (mmol g ⁻¹)	E (kJ mol ⁻¹)
AK-1	0.99	0.53	44.64	1.00	0.08	4.62	0.97	0.66	1.34
AK-2	0.97	0.74	28.98	0.91	0.07	4.17	0.97	1.42	0.80

The empirical Freundlich equation based on sorption on a heterogeneous surface is as follows [23–25]:

$$q_e = K_F \times C_e^{1/n} \quad (3)$$

This expression can be linearized to give

$$\log q_e = \log K_F + \frac{1}{n \log C_e} \quad (4)$$

where K_F and n are the Freundlich constants, which represent sorption capacity and sorption intensity, respectively. A plot of $\log q_e$ versus $\log C_e$ would result in a straight line with a slope of $(1/n)$ and intercept of $\log K_F$ as seen in Fig. 8.

According to isotherm models mentioned above, adsorption constants are calculated from the equations derived from the isotherm curves. The higher correlation coefficients showed that Freundlich model is suitable for AK-1 and Langmuir model is suitable for K-2 adsorption equilibrium of uranium in studied concentration ranges.

The sorption D-R isotherm model is applicable at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces. 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, ε , which is the free energy of the transfer of 1 mol of U(VI) ions from infinity to the surface of the sorbent. It can be represented by the general expression:

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (5)$$

where X_m is the maximum sorption capacity and β is a constant related to energy and ε is the Polanyi potential:

$$\varepsilon = RT \ln \left(\frac{1}{1 + C_e} \right) \quad (6)$$

where R is a gas constant in kJ mol⁻¹ and T is the temperature in Kelvin. If $\ln C_{ads}$ is plotted against ε^2 , β (mol K⁻¹)² and X_m (mmol g⁻¹) will be obtained from the slope and intercept, respectively. The sorption energy can also be worked out using the following relationship [26]:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

The constants of isotherms and correlation coefficient values of Langmuir, Freundlich and Dubinin-Radushkeviche (D-R) models were given in Table 2.

Table 3
Thermodynamic parameters for U(VI) sorption on Akaganeite as a function of temperature

Adsorbent	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)			
			293 K	30 K	313 K	323 K
AK-1	40.60	0.21	-20.93	-23.03	-25.13	-27.23
AK-2	24.88	0.16	-21.42	-23.00	-24.58	-26.16

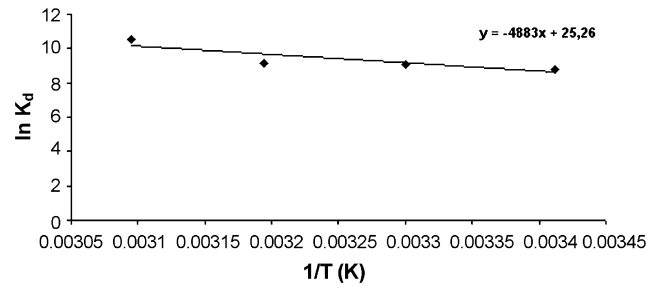


Fig. 10. A plot against $\ln K_d$ to $1/T$ for removal of U(VI) from AK-1.

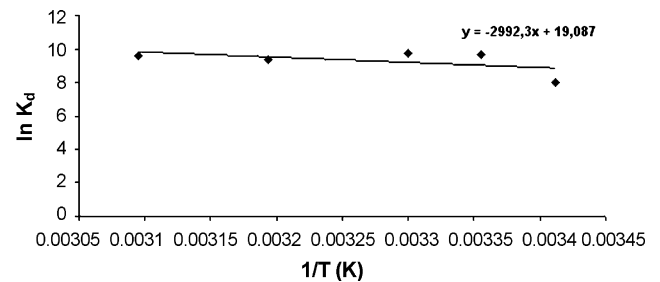


Fig. 11. A plot against $\ln K_d$ to $1/T$ for removal of U(VI) from AK-2.

3.6. Thermodynamic studies

The thermodynamic parameters obtained for the sorption process were calculated using equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

where K_d is the thermodynamic stability constant, ΔS° is standard entropy (J mol⁻¹ K⁻¹), ΔH° is standard enthalpy (kJ mol⁻¹), T is the absolute temperature (K) and R is the gas constant (8.314 J mol⁻¹ K⁻¹).

The adsorption processes were carried out 25–50 °C for U(VI) concentration of 100 and 150 mg L⁻¹ for AK-1 and AK-2, respectively. The values of ΔS° and ΔH° were evaluated from the slope and intercept in the diagram, Figs. 10 and 11. The standard Gibbs free energy (ΔG°) values (kJ mol⁻¹) were calculated from the equation:

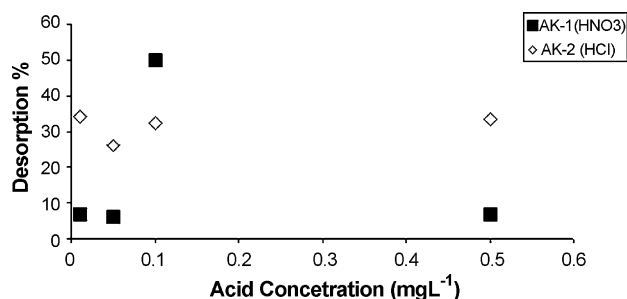
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

The values of ΔH° , ΔS° and ΔG° are reported in Table 3.

The positive values of ΔH° suggest the endothermic nature of adsorption of U(VI) ions on the AK-1 and AK-2. The negative values of ΔG° , indicate feasibility and spontaneous with the high preference of U(VI) for AK-1 and AK-2. The positive values of entropy show the increasing randomness at the solid/solution interface during

Table 4
Effects of some elution reagents for uranium desorption

Reagent	Desorption of AK-1 (%)	Desorption of AK-2 (%)
0.1 M HCl	10.50	6.87
0.1 M HNO ₃	50.07	6.52
0.1 M H ₂ SO ₄	8.23	6.70
0.1 M NaCl	1.28	0.86
0.1 M NaNO ₃	1.83	1.24
0.1 M NaOH	3.90	2.88
0.1 M CH ₃ COOH	1.30	2.00
Pure distilled water	2.55	2.04

**Fig. 12.** Effect of acid concentrations to desorption of U(VI).

the adsorption process. Also positive entropy of adsorption reflects the affinity of the adsorbent for U(VI). The adsorption is endothermic, therefore, the amount adsorbed at equilibrium must increase with increasing temperature, because ΔG° decreases with increasing temperature of the solution [27–31].

3.7. Desorption experiments

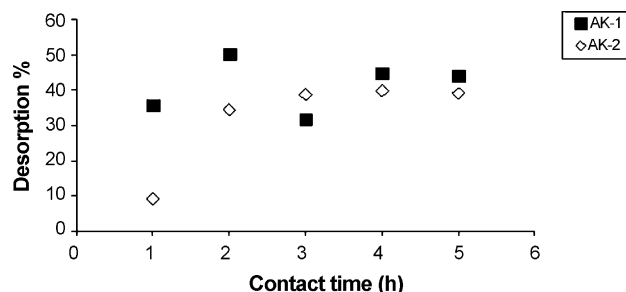
After 100 and 150 mg L⁻¹ of uranium had been adsorbed on AK-1 and AK-2, respectively, the adsorbents were treated with desorptive solutions to recover the adsorbed uranium from the adsorbents. Desorption of uranium was also performed by batch technique. Some desorptive reagents given in Table 4 were treated with loaded adsorbent to recover uranium from the adsorbent. As seen in Table 4, no significant uranium desorption with HNO₃ for AK-1 and HCl for AK-2 was observed. The desorption yields were lower with other desorptive reagents. Other desorption parameters were investigated to increase the desorption yield.

3.7.1. Effect of desorptive reagent concentration

Akaganeite (AK-1) and (AK-2) (0.01 g) loaded with maximum amounts of the U(VI) of 100 and 150 mg L⁻¹, respectively. The uranium desorption from AK-1 and AK-2 was studied as a function of 0.01, 0.05, 0.1 and 0.5 M HNO₃ and HCl solution employing for 2 h shaking time at 30 °C. Fig. 12 shows the dependence of uranium desorption on HNO₃ and HCl concentration. Maximum desorption (50.07% for AK-1 and 34.45% for AK-2) is achieved from 0.1 M HNO₃ and 0.01 M HCl solution which is selected as a desorptive medium, respectively. The amount of uranium desorbed by AK-1 was maxi-

Table 6
Adsorption yields of the elements for akaganeite treated with acidic leach solution

Element	Initial concentration (mg L ⁻¹)	Adsorption yield of AK-1 (%) (at pH 2)	Adsorption yield of AK-1 (%) (at pH 4)	Adsorption yield of AK-2 (%) (at pH 2)	Adsorption yield of AK-2 (%) (at pH 4)
UO ₂ ²⁺	237.50	40.38	41.09	39.91	39.32
Ca ²⁺	784.40	52.62	53.08	55.90	55.02
Cu ²⁺	19.01	39.71	35.45	36.45	33.77
Mg ²⁺	217.10	59.22	58.72	60.06	59.83
Fe ²⁺	124.60	0.00	96.02	34.76	95.87
Al ³⁺	204.00	34.70	31.37	30.78	28.82

**Fig. 13.** Effect of contact time to desorption of U(VI).**Table 5**
Effect of desorption stage

Adsorbent	Desorption yield (%)		
	1 stage	2 stage	Total
AK-1	50.07	6.22	56.29
AK-2	34.45	2.98	37.43

mum at 0.1 M of HNO₃, whereas above and below 0.1 M, there was a decrease in uranium desorption.

3.7.2. Effect of desorption time

The uranium desorption from loaded AK-1 and AK-2 has been investigated as a function of equilibrium time in the range of 60–300 min. The results are given in Fig. 13. 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. The results of the effect of contact time to desorption is shown in Fig. 13.

3.7.3. Effect of desorption stage

Table 5 shows the desorption yields of uranium from AK-1 and AK-2 after several desorption stages. The uranium recovered from AK-1 and AK-2 with two desorption stages. The desorption yield for AK-1 and AK-2 was decreased with increasing the desorption stages. After two desorption stages, 56% and 37% of the initially sorbed uranium were desorbed on AK-1 and AK-2, respectively and 50% of U(VI) desorbed from AK-1 in the first stage.

3.8. Applications of akaganeite adsorbents

As mentioned above, the adsorbents can take up uranium from the aqueous solution containing only uranium. However, the uranium uptake decreases when the adsorbents are treated with solution containing matrix elements. To determine the matrix effect on the uranium uptake, 10 mL of synthetic matrix solution and leach solution which was obtained from ore samples taken from Koprubasi-Manisa district in Western Aegean Region in Turkey (pH 2.0) and its adjusted optimum adsorption condition (pH 4.0 and pH 6.0) of AK-1 and AK-2, respectively were treated with 0.01 g of AK-1 and AK-2. The initial leach solution and the treated

Table 7
Adsorption yields of the elements for akaganeite treated with synthetic matrix solution

Element	Initial concentration (mgL ⁻¹)	Adsorption yield of AK-1 (%)	Adsorption yield of AK-2 (%)
UO ₂ ²⁺	40	20.91	9.35
Al ³⁺	20	4.32	3.00
Cd ²⁺	20	0.00	0.00
Cu ²⁺	20	7.54	12.97
Fe ²⁺	20	1.75	1.80
Ni ²⁺	20	4.00	7.68
Pb ²⁺	20	25.31	15.54

leach solutions with adsorbents were analyzed for uranium and other matrix elements. Table 6 shows the adsorption yields of uranium and other matrix elements onto adsorbents. The elements in the leaching solutions were analyzed by Perkin Elmer Optima 2000 DV ICP-OES.

For both of the adsorbents, adsorption yield of U(VI) is nearly 40%. Mg is better sorbed on AK-1 and AK-2 stronger than Al, Ca and Cu. The general belief is that iron (III) hydroxide precipitation begins at a pH of about 2.2 and is complete at a pH of 3.3. Iron precipitation begins at low pH values. If pH is neutral or higher, iron precipitation is probably the most important quantity. It explains that why iron adsorption yield is high at pH 4 about 96%. According to results, adsorption of U(VI) from matrix leach solutions by akaganeite is higher than similar literatures [32].

Uranium sorption from the synthetic matrix medium on the adsorbents was studied by batch technique. This synthetic matrix solution includes 40 mgL⁻¹ of UO₂²⁺ and 20 mgL⁻¹ of Pb²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Fe²⁺, Al³⁺ cations. A known weight (0.01 g) of AK-1 and AK-2 was equilibrated with 10 mL of synthetic matrix solution at pH 4.0 and pH 6.0 for 2 and 1 h at 25 °C for AK-1 and AK-2, respectively. The amounts of the metals in the solution were determined by ICP-OES. The results are given in Table 7.

The results show that adsorption yields are quite low for both of the adsorbents. The results for leach solution and synthetic matrix solution indicated that element concentration is very important for adsorption process on the adsorbents. Adsorption yield on the adsorbents is decreased with decreasing elements concentrations.

4. Conclusion

According to the results obtained in the study of the adsorption of uranium(VI) onto akaganeite, it can be concluded that AK-1 and AK-2 which are synthesized with two different methods and different precipitating agents can be used as an adsorbent for removal of low concentration U(VI) from aqueous solutions. AK-1 has a higher adsorption capacity than AK-2. The maximum U(VI) removal in AK-1 was obtained as >99% at pH 4.0 ± 0.1 at initial concentration of 50 mgL⁻¹ and amount of akaganeite equal to 0.01 g.

The experimental results have been analyzed by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms. The main energy of adsorption $E_{ad} = 1.34$ and 0.80 kJ mol⁻¹ was calculated from the D-R adsorption isotherm. The application of the Langmuir and Freundlich models to experimental results showed that the adsorption equilibrium data of AK-1 and AK-2 fitted to Freundlich and Langmuir.

Various thermodynamic parameters, such as ΔG° , ΔH° and ΔS° , were calculated from the experimental data. The thermodynamics of U(VI) ion/akaganeite system indicate spontaneous and endothermic nature of the process.

Desorption of metal ions from adsorbent was performed in low acid concentrations. The quantitative desorption of uranium from both adsorbents is quite difficult. The adsorbents can be used for the quantitative removal of uranium from aqueous solutions.

Adsorption of U(VI) onto AK-1 and AK-2 from synthetic and acidic leach solutions is also performed. It is found that the amount of uranium adsorbed differs markedly depending on the matrix elements and medium. It has been shown that the uptake of uranium from aqueous solutions by the adsorbents varies with the chemical species of uranyl ion and competitor ions in the medium.

The experimental studies showed that akaganeite could be used as an economic, effective and low-risk sorbent material to remove toxic and radioactive U(VI) ions from wastewaters.

References

- [1] R. Han, W. Zou, Y. Wang, L. Zhu, Removal of uranium (VI) from aqueous solutions by manganese oxide coated zeolite: discussion of adsorption isotherms and pH effect, *J. Environ. Rad.* 93 (2007) 127–143.
- [2] A. Mellah, S. Chegrouche, M. Barkat, The removal of uranium (VI) from aqueous solutions onto activated carbon: kinetic and thermodynamic investigations, *J. Colloid Interface Sci.* 296 (2006) 434–441.
- [3] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, Sorption of As(V) ions by akaganeite-type nanocrystals, *Chemosphere* 50 (2003) 155–163.
- [4] H. Parab, S. Joshi, N. Shenoy, R. Verma, A. Lali, M. Sudersanan, Uranium removal from aqueous solution by coir pith: equilibrium and kinetic studies, *Biores. Tech.* 96 (2005) 1241–1248.
- [5] A. Kılıncarslan, S. Akyil, Uranium adsorption characteristic and thermodynamic behaviour of clinoptilolite zeolite, *J. Radioanal. Nucl. Chem.* 264 (2005) 541–548.
- [6] S. Aytas, S. Akyil, M. Eral, Adsorption and thermodynamic behavior of uranium on natural zeolite, *J. Radioanal. Nucl. Chem.* 260 (2004) 119–125.
- [7] T.S. Psareva, O.I. Zakutevskyy, N.I. Chubar, V.V. Strelko, T.O. Shaposhnikova, J.R. Carvalho, M.J.N. Correia, Uranium sorption on cork biomass, *Colloid Surf. A: Phys. Eng. Aspects* 252 (2005) 231–236.
- [8] T. Missana, M. Garcia-Gutierrez, C. Maffiotte, Experimental and modelling study of the uranium (VI) sorption on goethite, *J. Colloid Interface Sci.* 260 (2003) 291–301.
- [9] N.S. Awwad, A.A.M. Daifullah, Preconcentration of U(VI) from aqueous solutions after sorption using Sorel's cement in dynamic mode, *J. Radioanal. Nucl. Chem.* 264 (2005) 623–628.
- [10] U. Schwert-Mann, R.M. Cornell, Iron Oxides in the Laboratory, VCH Publishers, New York (1991), *J. Solid State Chem.* 98 (1992) 442.
- [11] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sahane, K. Ooi, T. Hirotsu, Phosphate adsorption on synthetic goethite and akaganeite, *J. Colloid Interface Sci.* 298 (2006) 602–608.
- [12] G.A. Waychunas, C.S. Kim, J.F. Banfield, Nanoparticulate iron oxide minerals in soils and sediments: unique properties and contaminant scavenging mechanisms, *J. Nanopart. Res.* 7 (2005) 409–433.
- [13] H.F. Shao, X.F. Qian, J. Yin, Z.K. Zhu, Controlled morphology synthesis of β -FeOOH and the phase transition to Fe₂O₃, *J. Solid State Chem.* 178 (2005) 3130–3136.
- [14] Z.Y. Yuan, B.L. Su, Surfactant-assisted nanoparticle assembly of mesoporous β -FeOOH (akaganeite), *Chem. Phys. Lett.* 381 (2003) 710–714.
- [15] D.N. Bakoyannakis, E.A. Deliyanni, A.I. Zouboulis, K.A. Matis, L. Nalbandian, Th. Kehagias, Akaganeite and goethite-type nanocrystals: synthesis and characterization, *Micropor. Mesopor. Mater.* 59 (2003) 35–42.
- [16] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, Sorption of As(V) ions by Akaganeite-type nanocrystals, *Chemosphere* 50 (2003) 155–163.
- [17] T.M. Florence, AAEC/TM552, Paper 5, 1970.
- [18] C.A. Francois, Rapid spectrophotometric determination of submilligram quantities of uranium, *Anal. Chem.* 30 (1958) 50–54.
- [19] N. Kabay, Modifiye edilmiş polimerik amidoksin reçinelerin deniz suyundan uranyum kazanımına uygulanabilirliğinin incelenmesi, E.U. Reserach Foundation Project, Project No: 93 NBE 003, 1994 (in Turkish).
- [20] Report of Sarıcaoğlu Region for Uranium exploration, a Project of T.R. State Planning Organisation, Research grant Number 83 H00012, Institute of Nuclear Sciences, 1987.
- [21] M. Eral, S.R. Kinacı, *Spectrosc. Lett.* 22 (1989) 867–885.
- [22] R. Uzmen, K. Cımcım, H. Kopuz, Kasar ve Tasharman uranyum cevherleri üzerine teknolojik çalışmalar, in: Türkiye'nin Uranyum ve Toryum Kaynaklarının Değerlendirilmesi Semineri, 23–26 May, 1983, p. 52 (in Turkish).
- [23] S. Chegrouche, A. Mellah, S. Telmoune, Removal of lanthanum from aqueous solutions by natural bentonite, *Water Res.* 31 (1997) 1733–1737.
- [24] A. Boualia, A. Mellah, T.T. Aissaoui, K. Menacer, A. Silem, Adsorption of organic matter contained in industrial H₃PO₄ onto bentonite: batch-contact time and kinetic study, *Appl. Clay Sci.* 7 (1993) 431–445.
- [25] A. Mellah, S. Chegrouche, The removal of zinc from aqueous solutions by natural bentonite, *Water Res.* 31 (1997) 621–629.
- [26] S.M. Hasany, M.M. Saeed, M. Ahmed, Sorption and thermodynamic behavior of zinc (II)-thiocyanate complexes onto polyurethane foam from acidic solutions, *J. Radioanal. Nucl. Chem.* 252 (2002) 477–484.
- [27] E.A. Deliyanni, L. Nalbandian, K.A. Matis, Adsorptive removal of arsenites by a nanocrystalline hybrid surfactant-akaganeite sorbent, *J. Colloid Interface Sci.* 302 (2006) 458–466.

- [28] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, *J. Hazard. Mater.* 122 (2005) 161–170.
- [29] O. Yavuz, Y. Altunkaynak, F. Guzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, *Water Res.* 37 (2003) 948–952.
- [30] C.K. Jain, D.C. Singhal, M.K. Sharma, Adsorption of zinc on bed sediment of River Hindon: adsorption models and kinetics, *J. Hazard. Mater.* B114 (2004) 231–239.
- [31] I.N. Levine, *Physical Chemistry*, third ed., McGraw-Hill, New York, 1988.
- [32] S. Akyil, M.A.A. Aslani, M. Eral, Sorption characteristic of uranium onto composite ion exchangers, *J. Radioanal. Nucl. Chem.* 256 (2003) 45–51.