Uranium adsorption characteristic and thermodynamic behavior of clinoptilolite zeolite

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Natural zeolite, clinoptilolite was tested for its ability to remove uranium from aqueous solutions. Influence parameters to the sorption process, such as initial uranium concentration, pH, contact time and temperature were investigated. Distribution coefficients of uranium on clinoptilolite were measured by batch technique. Experimental isotherms evaluated from the distribution coefficients were fit to Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models. Values of ΔH and ΔS were found as 0.93 and 56.09 J/mole, respectively. It was observed that the adsorption process is endothermic. Kinetics of uranium sorption was investigated at different time intervals at 30 °C. The reaction rate and diffusion constant were calculated.

Introduction

One of the most effective methods for treatment and disposal of radioactive wastes has been based on adsorbents and ion-exchangers. The desirable characteristics of high exchange capacity and favorable selectivity for some radionuclides have made certain zeolites quite useful for the treatment of radioactive wastes.[1,2]

It is well known that natural zeolites are aluminosilicates of alkaline and alkaline earth cations with high chemical and radiation stability. Natural and synthetic zeolites have been used for treatment of radioactive waste solution, MLLW and HLLW result from nuclear fuel cycle,[3–6] for recovery and removal of the radionuclides from aqueous solutions and wastes.[7–13] Zeolites are relatively abundant in westeast of Turkey. An 18 million ton reserve of natural zeolite is spread over in Gordes-Manisa, Turkey. We used clinoptilolite taken from this area as an adsorbent.

The longevity actinide elements are important in the geological disposal of radioactive wastes. Uranium is a representative actinide element that is of fundamental importance in the nuclear fuel cycle, where it starts as a source and ends up as a final waste component. It is highly mobile and migrates as uranyl ion (UO_2^{2+}) and various soluble uranyl complexes under near surface conditions. It is, therefore, a potentially hazardous pollutant to the environment.[14] In this work, uranium was selected as a sorbate because of its relatively well-known chemistry among actinides and environmental significance of its own.

The purpose of this work is to investigate the ability of clinoptilolite to remove uranium from aqueous solutions testing the influence of specific process parameters, and to calculated the thermodynamic parameters such as free energy ($\Delta G°$), enthalpy of adsorption ($\Delta H°$) and entropy ($\Delta S°$). The applications of the isotherm models have been studied to explain the adsorption characteristics of the clinoptilolite. The adsorption equation best describing data obtained was determined.

Experimental

Materials and metod

Natural zeolite clinoptilolite, Manisa-Gördes was obtained from Pamukkale University, Faculty of Science and Literature, Department of Chemistry, Denizli-Turkey. Physical and chemical properties of the clinoptilolite reported by KARAPINAR,[15] in 1998 are given in Table 1. According to the XRD patterns of zeolite, it was obvious that the major phase in zeolite was clinoptilolite mineral (up to 70%) with plagioclase, mica, quartz, smectite, K-feldspar and chlorite.[15]

The natural zeolite was ground and sieved, and was used as size of –200 mesh for the adsorption experiments. $UO_2(NO_3)\cdot 6H_2O$ and PAR (1,2-pyridylazo resorcinol) were obtained from Merck Co. All other reagents used in this study were of analytical grade and were purchased from Merck. The buffer solutions (pH 4, 7 and 9) to calibrate the pH-meter Model 8521 from Hanna Instruments were also purchased from Merck.

Adsorption experiments

The sorption experiments have been studied by batch technique in 15-ml polyethylene tubes. The batch technique was carried out in a thermostated shaker bath Model GFL-1083. The shaking rate was the same for all experiments. The pH of the solution was adjusted prior to the experiments by adding a small amount of Na_2CO_3/HNO_3. The clinoptilolite (0.1 g) and

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Table 1. Chemical and physical properties of zeolite[15]

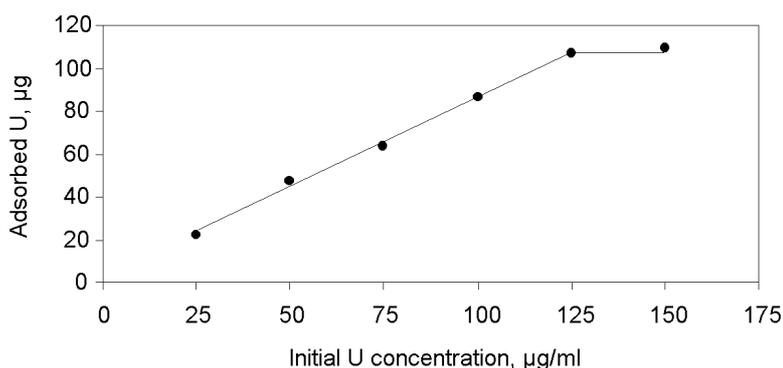| Chemical properties		Physical properties	
SiO_2, %	69.31	Porosity, %	41.5
Al_2O_3, %	13.11	Density, g/cm^3	2.27
Fe_2O_3, %	1.31	pH	7.50
CaO, %	2.07	Colour	white (68%)
MgO, %	1.13	Water absorption (for original), %	31.3
Na_2O, %	0.52	Water absorption (for granule), %	103.7
K_2O, %	2.83		
H_2O, %	6.88		
Si/Al	4.66		

Fig. 1. Sorption of uranium on clinoptilolite as a function of initial uranium concentration

$UO_2(NO_3)_2$ aqueous solution were shaken at different temperatures for various contact time. The uranium was determined spectrophotometrically using 1,2-pyridylazo resorcinol (PAR) as complexing agent at 510 nm against reagent blank, employing Shimadzu UV-VIS 260 spectrophotometer.[16] 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 zeolite and changing one parameter and keeping other parameters constant. The experiments were carried out in duplicate. Each experimental result was obtained by averaging the data from two parallel experiments.

Distribution coefficients, K_d, are traditionally used in nuclear waste disposal performance assessment to describe sorption of radionuclides.[17] Distribution coefficients are defined as the ratio of the concentration of the uranium in the sorbent and in the solution at equilibrium. The distribution coefficients and adsorption yield (%) were calculated by:

$$K_d = [(C_i - C_e)/C_e] \cdot V/m \ \ ml/g$$

$$\text{Adsorption yield (\%)} = [(C_i - C_e)/C_i] \cdot 100$$

where C_i is the concentration of the initial solution (µg/ml), C_e is the concentration of the solution in equilibrium (µg/ml), V is the volume of the solution (ml), m is the amount of the adsorbent (g).

Results and discussion

Effectual parameters on uranium sorption onto clinoptilolite

Sorption of U(VI) ions onto the clinoptilolite was studied as a function of the initial concentration of U(VI), pH of the adsorptive solution and contact time.

Effect of the initial uranium concentration: One of the most important parameters on the sorption system, which can influence the sorption behavior of uranium is the uranium concentration. To investigate of influence of the initial uranium concentration on uranium removal from the aqueous solution, tests were made under the following conditions: a pH of 5, uranium solution concentration ranging from 25 to 175 µg/ml, contact time of 180 minutes and V/m ratio of 100 at 30 °C. Figure 1 shows the amount of adsorbed U(VI) on the clinoptilolite.

The amount of adsorbed uranium on the clinoptilolite was increased with increasing initial uranium concentration in the solution. In the diluted solutions, the mobility of uranyl ions (UO_2^{2+}) is high, probably for this reason, the interaction of this ion with the adsorbent was increased. It was observed that the adsorbent reached the saturation in solution concentration of 125 μg/ml. On the basis of these results, 125 μg of uranium amount for clinoptilolite was used for all further studies.

Effect of pH: The pH of solution is an important variable for the adsorption of radionuclides on the adsorbents, and influences the metal speciation and surface metal binding sites. The effect of pH on uranium sorption was investigated ranging from 2 to 9, while keeping all other parameter constant. Figure 2 shows the influence of pH on the adsorption of UO_2^{2+} on the clinoptilolite. The sorption behavior in this study suggested the existence of a sorption mechanism that is strongly pH dependent and is favored by weakly acidic value. This figure indicates that the adsorption of UO_2^{2+}

ions increased with increasing pH up to pH 5 and then started decreasing at higher pH values. Further increase in pH resulted in the formation of the insoluble precipitate in the aqueous solution. Maximum adsorption occurs at pH 5. The behavior of UO_2^{2+} ions in aqueous solution is a complex phenomenon in the sense that UO_2^{2+} ions may be present as ions of different composition. U(VI) basically exists as free uranyl ion, its hydrolysis complexes, and multinuclear hydroxide and carbonate complexes as a function of pH and U(VI) concentration under experimental conditions. Free uranyl ion is the dominant species acidic pH range up to 6, UO_2OH^+ in the range of pH 5, $UO_2(CO_3)_3^{4-}$ in the range of pH higher than 7. From pH 4 to pH 8 the predominant uranium complex would be the neutral $UO_2CO_3^0$.[18] The increase in uranium sorption on the clinoptilolite above pH 5 is the result of the stable $UO_2CO_3^0$, $UO_2(CO_3)_3^{2-}$ and/or $UO_2(CO_3)_3^{4-}$ ions which are dominant complex ions at alkaline pH. The working pH for the next parameter was chosen as 5.
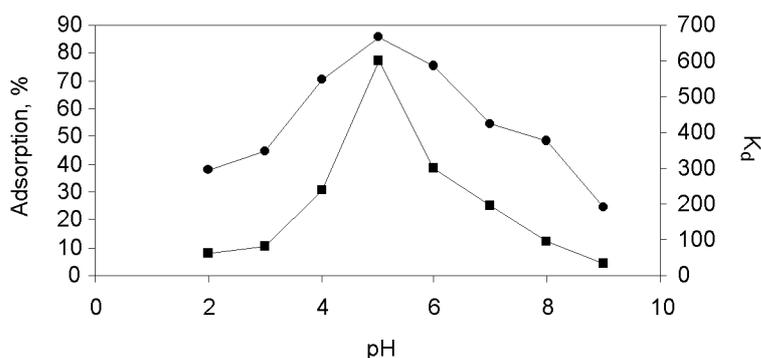

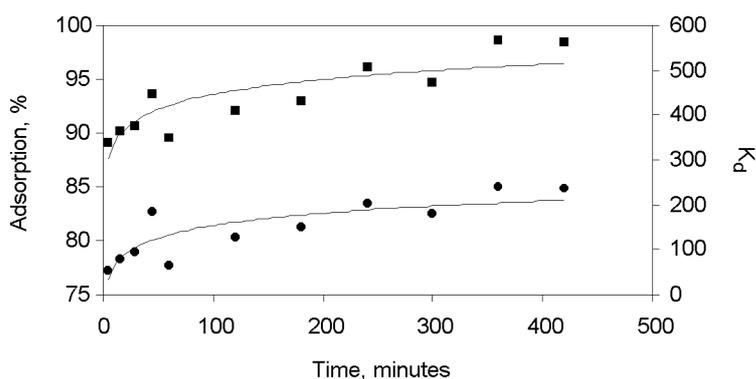*Fig. 2.* Influence of pH on the adsorption of U(VI) on clinoptilolite (● adsorption, ■ K_d)

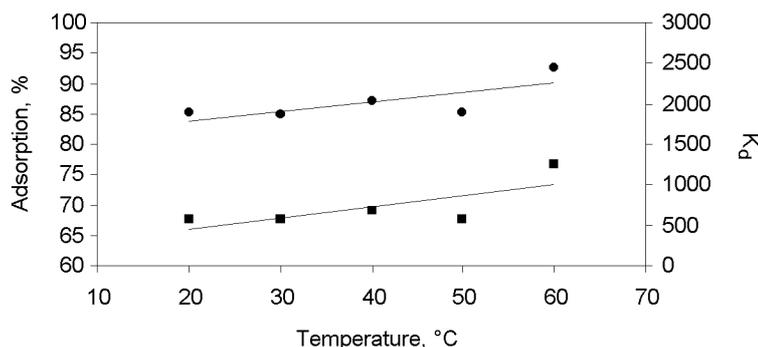*Fig. 3.* Effect of contact time on uranium sorption on clinoptilolite (● adsorption, ■ K_d)

Fig. 4. Effect of temperature on uranium sorption on clinoptilolite (● adsorption, ■ K_d)

Effect of contact time: For the evaluation of sorption as a function of contact time, from 5 minutes to 420 minutes contact intervals, were applied for the clinoptilolite. At the end of each contact interval, the distribution coefficients and adsorption yields for adsorbed uranium on the clinoptilolite were determined. The results are shown in Fig. 3. As shown in Fig. 3, the uranium sorption was increased with increasing contact time and reached equilibrium within 120 minutes. The uranium sorption by the adsorbent reached a plateau after this contact interval. A 120 minute shaking period was selected for all further studies.

Effect of temperature: The temperature dependant data were obtained by varying temperature from 20 to 70 °C while the other parameters were kept constant. Effect of temperature was shown in Fig. 4. It was observed that the uptake of uranium was increased with increasing temperature from 20 to 70 °C. It has been reported that such increase in the uptake might be due to the acceleration of some originally slow adsorption steps or due to creation of some new active sites on the surface of the adsorbent or due to transport against a concentration gradient and/or diffusion controlled transport across the energy barrier.[19]

Adsorption isotherms

Several common sorption isotherm models including Langmuir, Freundlich and Dubinin-Radushkevich (D-R) were considered to fit the data for sorption of uranium on clinoptilolite. The aim to compare the different adsorption models was to describe the adsorption of uranium on clinoptilolite.

The Langmuir and Freundlich models are widely used since they are simple and have an ability to describe experimental results in wide ranges of concentrations. Both isotherms can be easily transformed into linear forms to obtain adjustable parameters just by graphical means or by linear regression analysis. The Langmuir isotherm is used for homogeneous surfaces, and to handle nonhomogeneous surfaces, new isotherms were derived starting with Langmuir isotherms.

The applications of the Langmuir and Freundlich models have been further extended considering the influence of adsorption sites and the competition between different ions for adsorption on the available sites.

The Langmuir adsorption isotherm was tested in the following linearized form:

$$C_e/C_{ads} = (1/Q \cdot b) + (C_e/Q)$$

where C_e is the equilibrium concentration of uranium in solution and C_{ads} is the amount of uranium sorbed onto zeolite, Q and b are Langmuir constant related to sorption capacity and sorption energy, respectively.[20] A linear plot is obtained when C_e/C_{ads} was plotted against C_e over the entire concentration range of uranium(VI) investigated as shown in Fig. 5. From the slope and intercept of this plot the values of $Q=5.17 \cdot 10^{-3}$ mmol·g^{-1} and $b=27.45$ l·g^{-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.

Although the Freundlich isotherm is empirically based, it has proven useful for describing sorption that exhibits complex interactions between surface-binding sites and bound sorbate. It also can represent the situation in which bound sorbate molecules interact with each other, such as through hydrophobic or multi-layer effects.[21] The sorption data were tested on the following linearized from of Freundlich sorption isotherm:

$$\log C_{ads} = \log C_m + 1/n \log C_e$$

where C_{ads} is the amount adsorbed uranium (mmol·g^{-1}), C_e is the uranium concentration at equilibrium (mmol/l), $\log x/m$ and $1/n$ are the Freundlich constants referring to adsorption capacity and intensity of adsorption,

respectively. Figure 6 is shown the plot $\log x/m$ versus $\log C_e$. From the slope and intercept of straight portion of the plot the values of Freundlich parameters, i.e., $1/n$ and C_m are computed to be $1/n = 0.52$ and $C_m = 7.27 \cdot 10^{-4}$ mmol·g^{-1}. These values signify the sorption intensity and capacity, respectively. This 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 and suggests multiple binding sites, with the highest strength sites binding the sorbate first. Alternately, $1/n > 1$ can mean that bound sorbate molecules interact in such a way that the binding strength is increased as more sorbate binds.[21,22] 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.

The sorption data have been applied to D-R model. This is postulated within an adsorption space close to sorbent surface. The D-R equation was examined in the following linearized form:

$$\ln C_{ads} = \ln X_m - \beta \cdot \varepsilon^2$$

where C_{ads} is the amount adsorbed uranium (mol·g^{-1}), X_m is the maximum sorption capacity and β is the activity coefficient related to mean sorption energy and ε is Polanyi potential which is equal to:

$$\varepsilon = RT \ln(1 + 1/C_e)$$

where R is the gas constant in kJ·mol^{-1} and T is the temperature in Kelvin. The saturation limit (X_m) may represent the total specific micropore volume of the sorbent. The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate. The plot of $\ln C_{ads}$ versus ε^2 as shown in Fig. 7 is a straight line.
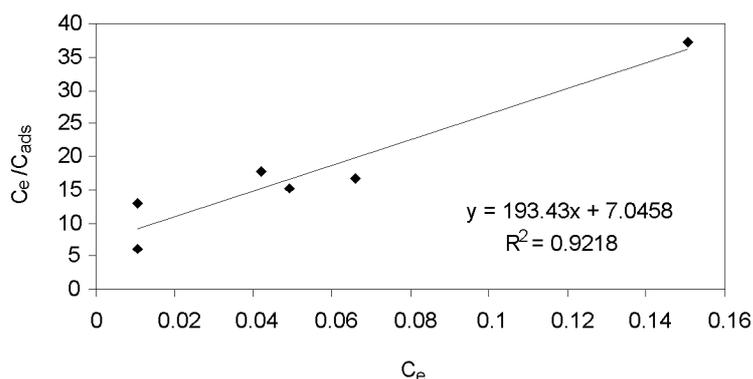
Fig. 5. Langmuir sorption isotherm of uranium onto clinoptilolite
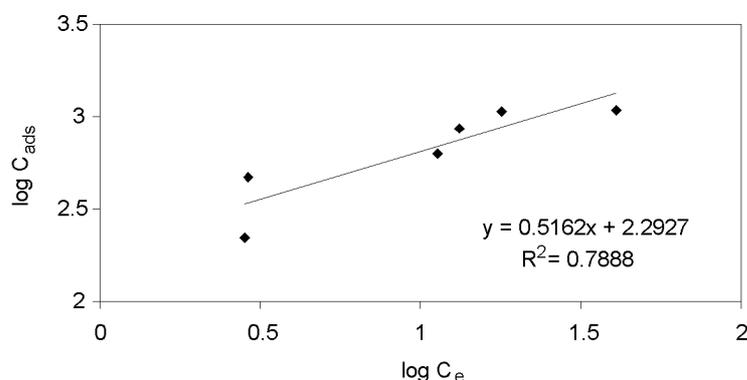
Fig. 6. Freundlich sorption isotherm of uranium onto clinoptilolite

From the slope and intercept of this plot the values of $\beta = -4 \cdot 10^{-9}$ mol$^2 \cdot$J^{-2} and of $X_m = 0.0338$ mmol$\cdot$g^{-1} have been estimated. The sorption energy can also be worked out using the following relationship:

$$E = 1/(-2\beta)^{-1/2}$$

The value of E for this system is estimated to be 11.18 kJ$\cdot$mol^{-1}.

Thermodynamics of the sorption process

The influence of temperature variation was examined on the sorption of uranium(VI) onto clinoptilolite using 120 minutes equilibration time and 125 µg/ml of sorptive solution from 20 to 70 °C. Thermodynamic parameters, i.e., heat of adsorption ($\Delta H°$) and entropy change ($\Delta S°$) for the sorption of U(VI) on clinoptilolite

were calculated for this system by:[23]

$$\ln K_d = (\Delta S°/R) - (\Delta H°/RT)$$

The plot of $\ln K_d$ versus $1/T$ is shown in Fig. 8. The values of $\Delta H°$ and $\Delta S°$ are obtained from the slope and intercept of the plot. The free energy for the specific adsorption ($\Delta G°$) was calculated by:

$$\Delta G° = \Delta H° - T\Delta S°$$

Thermodynamic parameters for the sorption process of uranium by natural zeolite are presented in Table 2. The positive value of $\Delta H°$ corresponds to the endothermic adsorption process. The numerical value of $\Delta G°$ decreases with increasing temperature as shown in Table 2. The negative values obtained for $\Delta G°$ indicate spontaneous nature of uranium sorption on clinoptilolite and more favorable at higher temperature. The positive entropy ($\Delta S°$) favors complexation and stability of sorption.
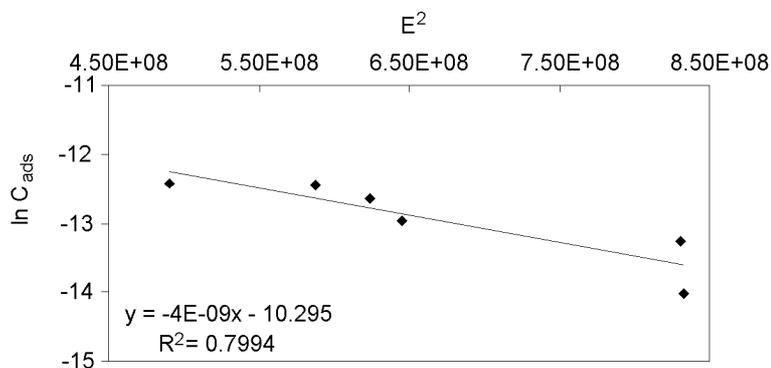

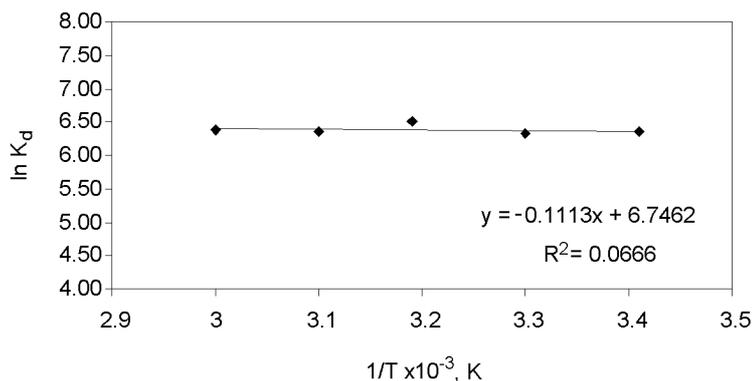*Fig. 7.* D-R sorption isotherm of uranium onto clinoptilolite

Fig. 8. Effect of temperature on uranium adsorption on clinoptilolite

Table 2. Thermodynamic parameters for adsorption on clinoptilolite as a function temperature

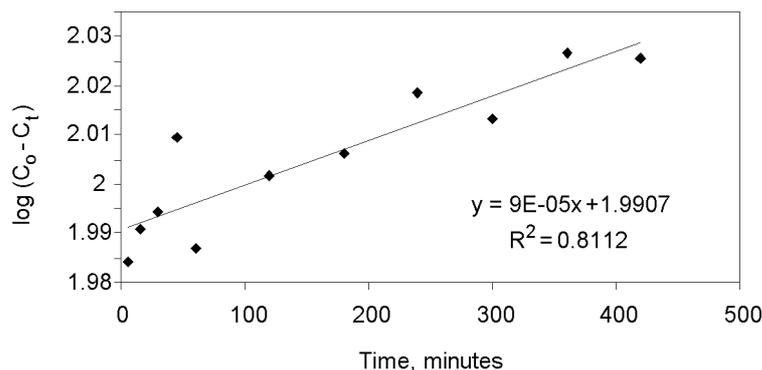| $\Delta H°$, J$\cdot$mol^{-1}	$\Delta S°$, J$\cdot$mol^{-1}	$\Delta G°$, kJ$\cdot$mol^{-1}				
		293 K	303 K	313 K	323 K	333 K
0.93	56.09	−16.44	−16.99	−17.56	−18.12	−18.68

Fig. 9. Kinetic experimental data for adsorption of uranium on clinoptilolite

Adsorption kinetics

In order to obtain information on the mass transfer and sorption kinetic, the curve was fitted using the sorption data obtained with the time effect. For the kinetic experiments, we took samples periodically to determine the time needed for sorption to reach equilibrium and analyzed for uranium concentration. Batch sorption experiments were performed at pH 5 with a fixed amount of adsorbent (0.1 g), and at uranium concentration of 125 μg/ml at 303 K. The kinetic experimental data are shown in Fig. 9. A linear plot is obtained when $\log(C_0-C_t)$ was plotted against time. From the slope and intercept of this plot, the reaction rate (k) and diffusion constant (D) at 303 K were found as $2.07 \cdot 10^{-4}$ min^{-1} and $1.14 \cdot 10^{-6}$ mm$^2 \cdot$min^{-1}, respectively.

Conclusions

The present work describes the sorption experiments of uranium from aqueous solution on a natural adsorbent, clinoptilolite. Uranium sorption onto clinoptilolite was investigated to determine the optimum conditions of pH, uranium concentration, contact time and temperature. The results of this work are that, under the optimum adsorption condition, uranium(VI) is significantly adsorbed as 82.9±1.9% by clinoptilolite, and show that the natural Turkish zeolite, clinoptilolite is economical and effective sorbent for uranium sorption and can be used to remove U(VI) from aqueous solutions.

The sorption data are followed Langmuir and D-R isotherms which indicate chemisorption and the value of the mean sorption energy (E) comes out to be 11.18 kJ·mol^{-1} reflecting its ion-exchange type nature. The data obeying Langmuir and D-R isotherms indicate transfer of uranium(VI) from aqueous solution to the surface of clinoptilolite as adsorption and bond formation between uranium(VI) and clinoptilolite may

be chemical in nature. The formation between uranium(VI) and clinoptilolite may be chemical in nature. The experimental data conform much better to the Langmuir isotherm than the Freundlich isotherm.

The positive value of $\Delta H°$ indicates endothermic and spontaneous nature of chemisorption. The negative values obtained for $\Delta G°$ show spontaneous nature of uranium sorption on clinoptilolite. Positive change in entropy favors a slower sorption of U(VI) onto active sites of the adsorbent. This conclusion is in agreement with the fact that uranium sorption attains an equilibrium within 120 minutes.

The adsorption kinetic was investigated for uranium sorption. The reaction rate and diffusion constant at 303 K were found as $2.07 \cdot 10^{-4}$ min^{-1} and $1.14 \cdot 10^{-6}$ mm$^2 \cdot$min^{-1}, respectively.

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