Journal of Alloys and Compounds 271/273 (1998) 769–773

Distribution of uranium on zeolite X and investigation of thermodynamic parameters for this system

Sema Akyıl*, Mahmoud A.A. Aslani, Şule (Ölmez) Aytaş

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

Abstract

The sorption of U(VI) from aqueous solutions on zeolite X has been studied by a batch technique. Distribution coefficients (K_d) were determined for sorption systems as a function of sorbate concentration, pH, contact time and temperature. The sorption isotherm was formed according to the Langmuir isotherm. Thermodynamic parameters have been determined at different temperatures. The $\Delta H°$ values for U(VI) on zeolite X were -29.5147 kJ mol^{-1} at 313 K at pH 3 and -19.8705 kJ mol^{-1} at 303 K at pH 9. The sorption of U(VI) on zeolite X is an exothermic in nature. Negative values of $\Delta G°$ show the spontaneous values for U(VI) that become less negative at higher temperatures, which shows that sorption is less favoured at higher temperatures. © 1998 Elsevier Science S.A.

Keywords: Zeolite; Zeolite X; Uranium adsorption; Adsorption isotherms

1. Introduction

Zeolites are crystalline aluminosilicates of alkali and alkaline earth cations. Zeolite frameworks are formed of SiO_4 and AlO_4 tetrahedra, which share all four corners. These can combine in many ways, giving rise to a large number of different zeolite structures. Exchangeable cations and water molecules are located in the channels of the framework. The general composition of zeolites can be represented by $M_{y/z}[(SiO_2)_x(AlO_2)_y]nH_2O$ where M is the exchangeable with a valency z. At least 70 different zeolite structures are known. In natural zeolites, the Si/Al ratio varies in the range of 1–6, and for most of the naturally occurring types, synthetic analogues have been prepared [1,2]. Zeolites with framework structures are excellent inorganic ion exchangers, having high stabilities to radioactive irradiation [3]. Zeolite exchangers have been widely studied and used in the full-scale separation of ^{137}Cs in waste solutions from nuclear power and fuel reprocessing plants. Harjula and Lehto have studied the effect of sodium and potassium ions on caesium adsorption from nuclear power plant waste solutions on synthetic zeolites [4]. Some zeolites, such as mordenite, chabazite and phillipsite, have been used for processing of radioactive liquid wastes, owing to their high ion-exchange capacity and selectivity for Cs [5]. Nardin et al. have reported on an investigation into the Pb behavior in zeolite X for removing Pb^{2+} from waste water, to limit the Pb^{2+} content in foods, and Pb-containing zeolites are used to improve industrial processes [6]. Langmuir (1926) gave the role of the solid surface in chemical reactions. He proposed that the molecules must be sorbed on catalyst surfaces by chemical bonds. At the present time this adhesion is well known as chemisorption. This phenomenon is different from physical adsorption, by which the molecules are attracted to the solid surface with Van der Waals forces [7].

The study of adsorption from liquid solutions by solid-phase expanded rapidly in the recent years. The recovery of uranium from aqueous systems, especially uranium mine waste from sea water, has received attention over the past three decades. Several conceptual and empirical models have been used to describe the equilibrium phase distributions for the sorption of uranium in surface systems [8–10]. The following linearized form of the Langmuir equation was used for this purpose

$$U_{eq}/y = (1/a) + (b/a) \times U_{eq} \tag{1}$$

where U_{eq} is the concentration of solute in the solution phase at equilibrium (g l^{-1}), y is the amount of solute sorbed per unit weight of sorbent (mg g^{-1}), and b and a are the Langmuir constants; b is represented as the ratio of adsorption and desorption rate coefficients (l g^{-1}),

$$a = b \cdot Q° \tag{2}$$

where $Q°$ is the maximum sorption capacity (mg g^{-1}). A

---

*Corresponding author: Fax: +90 232 3886466; e-mail: AKYILS@egeuniv.ege.edu.tr

PII: S0925-8388(98)00204-7

plot of U_{eq}/y against U_{eq} gives a straight line, the slope and intercept of which correspond to b/a and $1/a$, respectively. At low concentrations the Langmuir equation reduces to a linear relationship, while the maximum sorption capacity, $Q°$, is attained at concentrations corresponding to monolayer coverage. As the value of b becomes larger, the limiting sorption capacity is attained at lower solution phase concentration [11]. In the literature concerning uranium adsorption, the synthetic zeolites were limited to a narrow range and relatively few species were tested [12,13].

The present investigation was undertaken to obtain fundamental information on the adsorption of uranium using a synthetic zeolite. The adsorption behaviour of U(VI) on zeolite X has been studied under various experimental conditions, i.e. uranium concentration, pH, contact time and the effect of the temperature. Adsorption isotherms have been analysed in terms of the Langmuir equation. Thermodynamic parameters, such as enthalpy of adsorption, $\Delta H°$, free energy change, $\Delta G°$, and entropy change, $\Delta S°$, have been calculated and interpreted.

2. Experimental

In this work, the synthetic zeolite was used. After the zeolite X was synthesized, the molar ratio Si/Al was determined by measuring the Al and Si contents by AAS and Na by flame photometry [14]. The zeolite X was sieved through a −60 mesh screen. Zeolite X was used without any heating or other treatment for the sorption studies reported here. The standard uranium feed solution was prepared by dissolving of $UO_2(NO_3)_2 \cdot 6H_20$ (Merck, A.R.) in 1 ml of conc. HNO_3 and diluting with deionized water. The working solutions were prepared from the stock solution. Their pH was adjusted using nitric acid, sodium bicarbonate or sodium carbonate in such a way that the required pH was achieved from the acid side. All chemicals reagents used in the experiments are of analytical reagent grade without further purification. The sorption of U(VI) on zeolite X was studied by a batch technique with a magnetic stirrer. A known weight, 0.5 g, of the zeolite X was equilibrated, with 50 ml of the uranium solution of known concentration, at a fixed temperature in a water bath using a magnetic stirrer for a known period of time. After the equilibration process, the suspension was filtered by using Whatman filter paper No. 44. The solution/solid ratio in all these experiments was 100:1. The distribution coefficient, K_d (ml g^{-1}), of uranium was calculated from the following equation,

$$K_d = [(C_i - C_f)/C_f]V/m \quad (ml\ g^{-1}) \tag{3}$$

where C_i and C_f are concentrations of uranium in solution at the beginning and at the end of the sorption, respectively, V is the volume in ml of the solution used for equilibration, and m is the mass of adsorbent in grams. The percentage adsorption (%), was calculated from K_d using the following equation.

$$P = [(100xK_d)/(K_d + V/m)] \tag{4}$$

The amount adsorbed per unit weight of the zeolite X, x/m, was calculated from the initial and final concentrations of the solutions using the DBM method (dibenzoyl methane method, $\lambda = 395$ nm, molar absorbtivity 2.0×10^4 ($a = 0.0088$)) spectrophotometrically [15].

3. Results and discussion

3.1. Effect of uranium concentration

The sorption U(VI) on zeolite X as a function of their concentration was studied at 25±2°C, pH 8.0, by varying the metal concentration from 8×10^{-6} to 8×10^{-5} M, while keeping all other parameters constant. The result is shown in Fig. 1. The percentage adsorption of U(VI) decreases with increasing uranium concentration in the aqueous solution. In the diluted solutions, the mobility of uranyl ions (UO_2^{2+}) is high, for this reason, probably, the interaction of this ion with the adsorbent was increased. Iskikara et al. have reported the K_d values for uranium in zeolite A in the acidic (pH 4.17) and alkaline (pH 10.81) regions to be within the range of 26.05–28.60 and 28.74–45.62, respectively [12]. On the basis of these results, a 4×10^{-5} M concentration of U(VI) was used for all further studies.

3.2. Effect of pH on the sorption of uranium

The effect of pH on the sorption of uranium 4×10^{-5} M on zeolite X was studied by varying the pH of the solution–zeolite X suspension from 2 to 11 at 25±2°C. The zeolite X was dissolved below pH 2. The result is shown in Fig. 2. The K_d value for U(VI) decreases to pH 5, beyond which it increases very sharply. The percentage adsorption attains a 82% adsorption at pH 3 and 75% adsorption at pH 9, respectively. The uranium sorption was increased when the pH was increased from 6.0 to 9.0. The

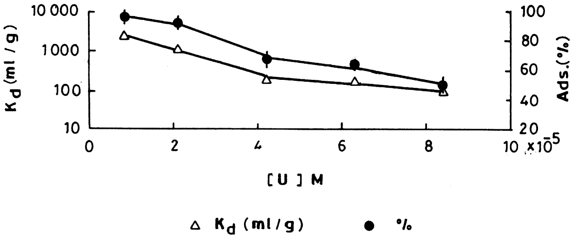

Fig. 1. Effect of U(VI) concentration on its sorption on zeolite X: temperature, 25±2°C; pH 8; contact time, 5 h; 0.5 g zeolite X; V, 50 ml.

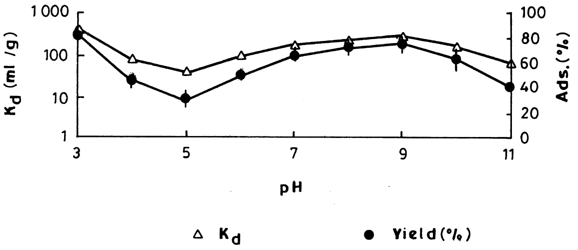

Fig. 2. Variation in K_d and percentage adsorption yield on Zeolite X as a function pH: temperature, 25±2°C; contact time, 5 h; 0.5 g zeolite X; [U], 4×10^{-5} M.

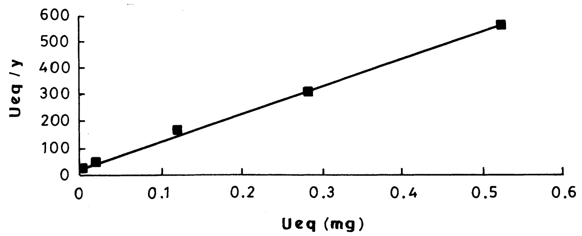

Fig. 4. Langmuir adsorption isotherm: $a=0.042$, $b=42.25$ l g^{-1}, $Q°=9.94\times10^{-4}$ mg g^{-1}, $r=0.999$.

uranium-containing oxygen compounds and the common uranyl (UO_2^{2+}) ion can combine easily with NO_3^-, and CO_3^{2-}. In an aerated aqueous solutions at pH≤2.5, the uranyl ion is very stable. Near pH 7, the uranyl ion forms stable complexes with carbonate. At pH 7–10, the soluble carbonate complexes of UO_2^{2+} are the predominant anion species $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. These two complexes exist in various ratios depending on the pH of the solution [16]. Therefore, as shown in Fig. 2, two maximum adsorption yields are observed at pH 3 and pH 9. Mimura et al. have studied the breakthrough properties of uranium for Y, A, X, M or L zeolite columns and investigated the breakthrough behavior in the acidic, neutral and alkaline regions [13].

3.3. Effect of contact time

The sorption of U(VI) on zeolite X was studied as a function of contact time at 25±2°C. Fig. 3 shows the variations of K_d and percentage adsorption with contact time for U(VI) at pH 3 and pH 9, respectively. In these pH mediums, the K_d and adsorption yield are not changed. The uranium adsorption is fast and attains equilibrium in 15 min after mixing.

3.4. Adsorption isotherm

The adsorption isotherm for U(VI) sorption on zeolite X was obtained at various uranium concentrations. Fig. 4 showing these results were analysed in term of Langmuir isotherm. The sorption data for U(VI) in the concentration range used was fitted in the Langmuir equation. And the values of a, b and $Q°$ were calculated from Eq. (1) and Eq. (2) as $a=0.042$, $b=42.25$ l g^{-1}, $Q°=9.94\times10^{-4}$ mg g^{-1}, respectively. The Langmuir isotherm dictates a limiting sorption capacity and, once monolayer coverage is achieved, sorption no longer significantly influences solute transport. Such behaviour is characteristic of Langmuir-type sorption, and can be attributed to a strong affinity of the solute for the solid phase at low concentrations (prior to attainment of monolayer coverage).

3.5. Thermodynamic parameters

Thermodynamic parameters, i.e. heat of adsorption, $\Delta H°$ and entropy change, $\Delta S°$, for the sorption of U(VI) on zeolite X were calculated for this system by using the following equation [17,18].

$$\ln K_d = (\Delta S°/R) - (\Delta H°/RT) \qquad (5)$$

The plots of $\ln K_d$ against $1/T$ for U(VI) for two different pH are shown in Fig. 5. The values of $\Delta H°$ and $\Delta S°$ are obtained from the slope and the intercept of each plot, which were calculated by a curve-fitting program [19]. The free energy for the specific adsorption, $\Delta G°$, was calculated by using the following well-known equation [17,18]

$$\Delta G° = \Delta H° - T\Delta S° \qquad (6)$$

The values of the thermodynamic parameters for the sorption of U(VI) on zeolite X are given in Table 1.

4. Conclusion

In the present work, we report kinetic studies on the adsorption of uranium by zeolite X at temperatures of 25

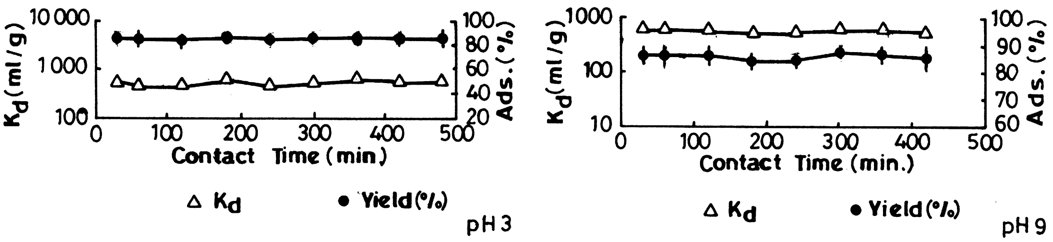

Fig. 3. Variation in K_d and percentage adsorption yield of U(VI) on zeolite X at pH 3 and pH 9 as a function of contact time: temperature, 25±2°C; 0.5 g zeolite X; [U], 4×10^{-5} M.

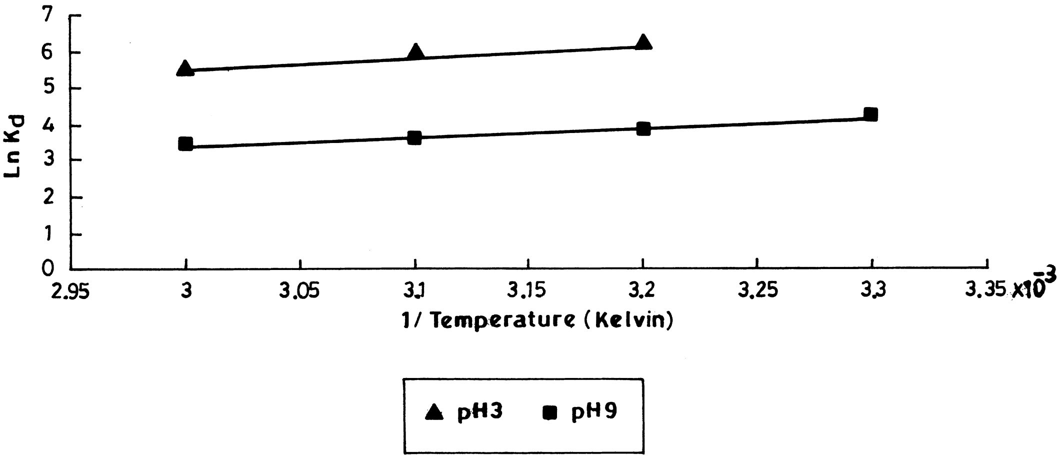

Fig. 5. The plot of $\ln K_d$ against $1/T$ for U(VI) at pH 3 and pH 9.

Table 1
Kinetic parameters for adsorption of U(VI) on zeolite X as a function temperature at pH 3 and pH 9

	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})			
			303 K	313 K	323 K	333 K
pH 3	−29.5147	−42.1520	—	−16.3211	−15.8996	−15.4781
pH 9	−19.8705	−31.5932	−10.2977	−9.9818	−9.6659	−9.3499

and 60°C. The results obtained allow the following conclusions.

The maximum sorption capacity was calculated as 9.94×10^{-4} mg g^{-1} zeolite X, and the reaction follows a linear form of the Langmuir model. The negative values of $\Delta H°$ show that the sorption of U(VI) on zeolite X is an exothermic process. The values of $\Delta G°$ for these processes become less negative with increasing temperature, which shows that sorption is less favoured at high temperatures. The decreases in the entropy, $\Delta S°$, in both of these processes in Table 1, show that the sorbate ions are stable on the solid surface. Association, fixation or immobilization of U(VI) ion as a result of adsorption is attributed to a decrease in the degree of freedom of adsorbate ion which results in the entropy change. It has also been shown that the adsorption of uranium in zeolite X varies with some factors such as uranium concentration, pH, contact time.

These results show that zeolite X can effectively be used if the metal concentration is low and adsorption with zeolite X can be successfully used to separate uranium from both acidic and basic solutions.

References

[1] R. Harjula, Ion exchange and hydrolysis reactions in zeolites, Rep. Ser. Radiochem. 8 (1993), pp. 1-40.
[2] C.B. Amphlett, Inorganic Ion Exchangers, Harwell, England, 1964.
[3] T. Kanno, H. Mimura, Ion exchange properties of zeolites and their application to processing of high level liquid waste, IAEA–TEC-DOC–337, 1985.
[4] R. Harjula, J. Lehto, Effect of sodium and potassium ions on cesium adsorption from nuclear power plant waste solutions on synthetic zeolites, Nucl. Chem. Waste Management 6 (1986) 133.
[5] H. Mimura, F. Tachibana, K. Akiba, Distribution and fixation of cesium in ferrierites, in: Proceedings III International Conference on Nuclear Fuel Reprocessing and Waste Management, 14–18 April, Atomic Energy Society of Japan, 1991, p. 796.
[6] G. Nardin, L. Randaccio, E. Zangrando, Lead clustering in a zeolite X, Zeolites 15 (1995) 684.
[7] A.R. Ghenberpour, Simple Kinetics of Reactions, Tehran University Press, Tehran, 1986.
[8] S. Nakamura, S. Mori, H. Yoshimuta, Y. Ito, M. Kanno, Uranium adsorption properties of titanium oxide granulated with polyacrilonitrile, Sep. Sci. Tech. 23(6–7) (1988) 731–743.
[9] Y. Ito, S. Nakamura, M. Shirakashi, M. Kanno, Uranium adsorption characteristics of a circulating fluidized-bed adsorber, AICHE J. 38(6) (1992) 879.
[10] L. Pietrelli, A. Salluzzo, F. Troiani, in: L. Cecille, M. Casarcs, L. Pietrelli (Eds.), New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications, Proceedings of a Technical Seminar, Elsevier, Amsterdam, 1991, pp. 87–105.
[11] W.J. Weber, K.D. Pennell, T.J. Dekker, L.M. Abriola, in: M. Aral (Ed.), Advances in Ground Water Pollution Control and Remediation, NATO-ASI, Kemer, Turkey, 1995, pp. 1–31.
[12] Y. Iskikara, H. Mimura, K. Akiba, Uranium adsorption characters in zeolite, Nucl. Sci. Res. 21(6) (1988) 71.
[13] H. Mimura, Y. Ishihara, K. Akiba, Breakthrough properties of uranium in zeolite columns, Res. Inst. Min. Dress. Met. 46(2) (1990) 105.
[14] S. Akyıl, Investigation of usability of zeolite X on uranium adsorption, M.Sc. Thesis, Ege University, Institute of Nuclear Sciences, Izmir, Turkey, 1991 (in Turkish).

[15] J. Korkish, Modern Methods for the Separation of Rare Metal Ions, Pergamon Press, Oxford, 1974, pp. 574–587.

[16] T. Sorg, in: C.R. Cothern, P.A. Rebers (Eds.), Radon, Radium and Uranium in Drinking Water, Lewis, USA, 1991, pp. 173–191.

[17] S.A. Khan, R. Rehman, M.A. Khan, Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite, Waste Management 15(4) (1995) 271.

[18] M. Saleem, M. Afzal, R. Qadeer, J. Hanif, Selective adsorption of uranium on activated charcoal from electrolytic solutions, Sep. Sci. Technol. 27 (1992) 239.

[19] J.P. Arkins, Curve Fits, version 4.27, 1993.