

Ion Exchange Behavior of Zeolites A and P Synthesized Using Natural Clinoptilolite

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ABSTRACT: *The main goal of this study is to investigate the capability of zeolites A and P synthesized from Iranian natural clinoptilolite for uranium uptake. The removal of uranium(VI) from aqueous solution via ion exchange by zeolites in a single component system with various contact times, temperatures and initial concentrations of uranium(VI) was investigated. The experimental results were fitted to the Langmuir and Dubinin-Radushkevich isotherms to obtain the characteristic parameters of each model. Both the Langmuir and Dubinin-Radushkevich isotherms were found to good represent the measured adsorption data. Using the thermodynamic equilibrium constants obtained at two different temperatures, various thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° have been calculated. The thermodynamics of uranium(VI) ion and zeolite system indicates the spontaneous and endothermic nature of the process. It was noted that an increase in temperature resulted in a higher uranium loading per unit weight of the adsorbent.*

KEY WORDS: *Ion exchange, Zeolite A, Zeolite P, Uranyl.*

INTRUDUCTION

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. Radioactive wastes occur at all stages of the nuclear fuel cycle. The cycle comprises the mining and milling of the uranium ore, its processing and fabrication into nuclear fuel, its use in

the reactor, the treatment of the spent fuel taken from the reactor after use and finally, disposal of the wastes. The fuel cycle is often split into two parts - the "front end" which stretches from mining through to the use of uranium in the reactor - and the "back end" which covers the removal of spent fuel from the reactor and its subsequent treatment and disposal. This is where radioactive wastes are a major issue. The long-lived radionuclides in other radioactive waste have been considered to be dangerous pollutants, and their migration with groundwater is strongly affected by

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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].

Management of radioactive wastes is an important issue for technical, social and political reasons. The so-called "legacy wastes" from nuclear fuel reprocessing wastes, medical and industrial isotope production wastes and spent fuel designated as waste by some countries pose current and pressing problems. All of these wastes must be safely managed and disposed of.

Various techniques are used for removal of dissolved uranium from surface waters, groundwater, and waste streams in order to prevent or environmental pollution. Ion exchange method is one of the most common methods that is used for removal of radionuclides from waste waters. Synthetic ion-exchange resins are commonly used to remove uranium from water [2]. However, the desirability of ion-exchange resins can be limited by the material costs, interferences by competing ions, poor extraction at low uranium concentrations, and the production of a large volume of waste when the exchange resin is disposed or the generation of a highly corrosive uranium-containing waste if the uranium is extracted from the resin.

Comparing with synthetic resins, zeolites have advantages that make them more applicable and useful for removal of radioactive cations [3-6]. Zeolites are, for example, more compatible with environment; they are stable at high temperatures and acidic and corrosive environments, they have potential selectivity toward some cations, natural zeolites are available and synthetic forms can be easily synthesized.

EXPERIMENTAL

Natural zeolites from two different regions of Iran (i.e. Semnan and Ardakan) were collected, ground and sieved. Both zeolites were clinoptilolite type. Some portions with the particle size of 224-500 μm were tested for ion exchange experiments. According to our primary experiments natural zeolites didn't show appropriate affinity toward the uranyl ion, so the synthetic zeolites, were synthesized and chosen for further experiments aimed at improving the ion exchange property.

Zeolites A and P (hereafter shown as Z-A and Z-P, respectively) were synthesized under hydrothermal

condition according to procedures explained in literatures [7, 8]. These zeolites were characterized using XRD, XRF methods. The results showed that the zeolites were successfully synthesized.

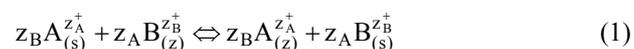
To evaluate the ion exchange properties of the zeolites, K_d for ion exchange was calculated. 0.2 g of each zeolite was exposed with 20 ml of uranyl nitrate solution for 24 hours. Filter-separating of solid phase from liquid was followed by centrifuging (5000 rpm for 30 minutes) in order to separate colloidal particles. A portion of supernatant was taken for uranyl measurement. The colorimetric method was carried out with Arsenazo(III) as a specific reagent for Uranyl determination using UV-Visible spectrophotometry (CARY 3) with 1.0 cm quartz cuvette at 652 nm and a pH range of 1.5 - 3.5.

The time required achieving the equilibrium was determined by the evaluation of K_d in different periods of time at uranyl concentration of 0.005 N (595 ppm). Temperature effect on K_d of sorption was investigated at four different temperatures.

The ion-exchange isotherms were obtained by analyzing iso-normal solutions in contact with zeolite powder and plotted in terms of the equivalent fraction of cation in the zeolite phase (A_z) against the equivalent fraction in the solution phase (A_s). Experimental isotherms were obtained at total normality of 0.005 N to keep the ionic strength of the solution constant. The total volume of the solutions was 20 ml and the isotherms were plotted at two different temperatures. The thermodynamic parameters of the ion exchange reaction (ΔG , K_a) were calculated by software compatible with Microsoft Excel [11].

Computation of Thermodynamic Exchange Parameters

The measured equilibrium data were plotted as ion exchange isotherms reporting the equivalent fraction of competing cations in solid phase as a function of the equivalent fraction of the same cations in solution. A general exchange reaction can be represented as:



Where A and B are two cations, z_A and z_B are valences of A and B, subscripts (s) and (z) denote solution and zeolite phase, respectively. The isotherms corresponding to ion exchange are normally expressed as

plots of A_s versus A_z . They may be calculated as:

$$A_s = C/C_0 \text{ and } A_z = (C_0 - C)/\text{CEC} \quad (2)$$

Where C stands for the final concentration of the in-going cation in the solution; C_0 stands for the sum of the initial concentration of the in-going cations and CEC is the cation exchange capacity of each zeolite mass.

The exchange isotherms data under known conditions can be used for determining the thermodynamic properties of exchange process. Thus, the selectivity coefficient is defined as:

$$K_c = A_{(z)}^{z_B} B_{(s)}^{z_A} / B_{(z)}^{z_A} A_{(s)}^{z_B} \quad (3)$$

Where A_z and B_z are the equivalent fractions of the in-going ion A and out-going B in the solid phase and a_A and a_B are mean activities of the same cations in solution associated with molality; z_A and z_B are the charge of the in-going ion A and out-going ion B , respectively.

Mean ionic activity coefficients in mixed solutions were evaluated from mean ionic activity coefficients calculated by Ciavatta's proposed method [7] and corrected by the Glueckauf's equation [8]. Kielland plot, $\log K_c$ versus A_z , is obtained by the selectivity quotient and may provide us information regarding the exchange mechanism. Non-linear plots are found due to distinct groups of exchange sites participating in the ion exchange process. Equilibrium constants, K_a , and standard free energies of exchange per equivalent of exchanger, ΔG° , were calculated according to the approach of Gaines and Thomas:

$$\log K_a = 0.4343(z_B - z_A) + \int \log K_c dA_z \quad (4)$$

$$\Delta G^\circ = \frac{RT}{z_A z_B} \ln K_a \quad (5)$$

The convex isotherms were also tested by Langmuir-type [9] and Dubinin-Radushkevich (D-R) [10] isotherms. The following Langmuir equation was used to describe the equilibrium data:

$$X_{A(z)} = kb_1 X_{A(s)} / (b_1 X_{A(s)} + b_2 X_{B(s)}) \quad (6)$$

Where X is the equivalent fraction of the cation (A or B) in the zeolite (Z) or solution (S) and k , b_1 and b_2 are constants. This approach, if valid, allows one to calculate the maximum degree of exchange of zeolite for the in-

going cation B . Indeed $X_{B(z)}=k$ when $X_{B(s)}=1$. Moreover the ratio $s=b_1/b_2 (= \beta/\alpha)$ is a measure of zeolite selectivity for B compared with A . k and b are the characteristics of the Langmuir equation; they can be determined from linearized form of Eq. (7):

$$\frac{X_{A(s)} / X_{B(s)}}{X_{A(z)}} = \alpha + \beta X_{A(s)} / X_{B(s)} \quad (7)$$

With $\alpha=b_2/kb_1$ and $\beta=1/k$. A plot of $(X_{B(s)} / X_{A(z)})/X_{B(z)}$ against $X_{B(s)}/X_{A(s)}$ should give a straight line. The D-R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$X_{B(z)} = X_m \exp(-K\varepsilon^2) \quad (8)$$

Where K is a constant related to the adsorption energy (mol^2/kJ^2), X_m is the theoretical saturation capacity per unit weight (mol/g), $X_{B(z)}$ is the amount of solute adsorbed per unit weight of solid (mol/g) and ε is the polanyi potential, equal to $RT(1+1/C)$ where C represents the equilibrium solute concentration (mol/l). The linear form of Eq. (9) is:

$$\ln X_{B(z)} = \ln X_m - K\varepsilon^2 \quad (9)$$

The mean energy of adsorption (E) can be calculated from the following equation:

$$E = (-2K)^{-1/2} \quad (10)$$

The magnitude of E is useful for estimating the type of adsorption process.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the kinetic curves of uranyl sorption on zeolites A ($Z-A$) and P ($Z-P$). Equilibrium of sorption for zeolite A is achieved in 10 hours and for zeolite P in 16 hours so the kinetic of exchange for zeolite A was faster than P . It could be attributed to the lower Si/Al ratio in zeolite A and higher cation exchange capacity of this zeolite. Another reason that could be a important factor is the particles size of zeolite A . Particle size of synthesized zeolite A were less than 30 micrometer, so the specific area of the zeolite was larger than zeolite P (particle size of zeolite P was as same as the precursor).

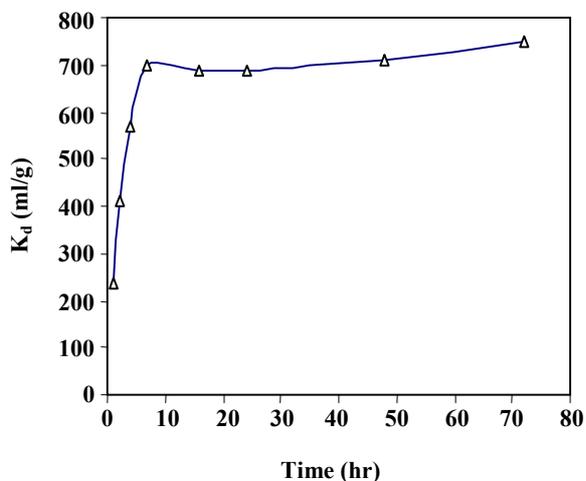


Fig. 1: Ion exchange rate of uranyl ion on zeolite A.

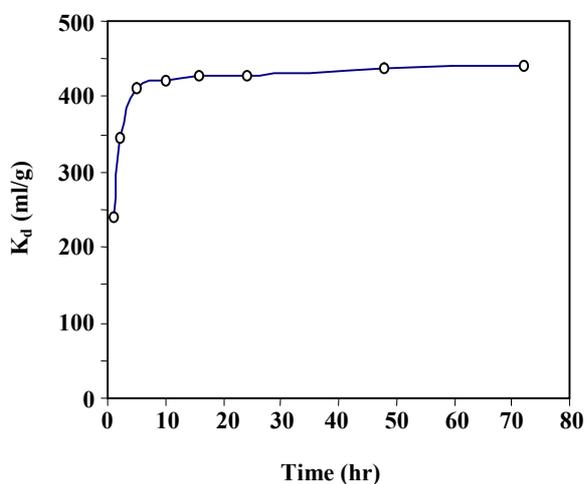


Fig. 2: Ion exchange rate of uranyl ion on zeolite P.

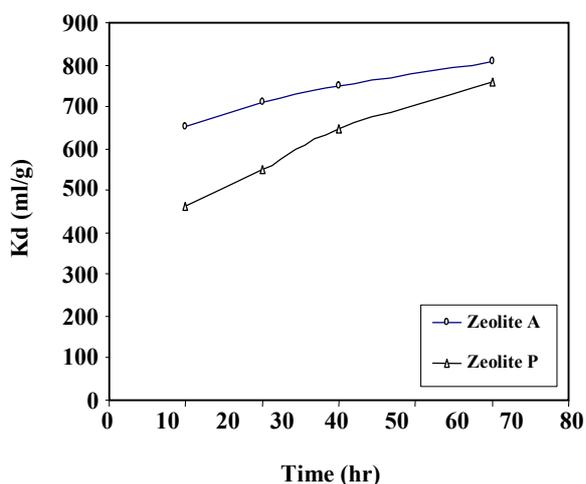


Fig. 3: Effect of temperature t on K_d .

Fig. 3 shows the effect of temperature on K_d . It is observed that value of K_d increases with increasing the temperature. The rise of K_d is due to the increase of ions mobility at higher temperatures and increase of diffusion rate. Increasing the temperature leads to more increase of K_d for zeolite P rather than zeolite A. Zeolites A and P have high and low specific areas, respectively, so increasing the temperature should have more effect on diffusion of the uranyl cations and their reaching to the exchange sites.

Figs. 4 and 5 are related to the isotherms of UO_2^{+2} exchange both for Z-A and Z-P at 25.0 °C and 50.0 °C with a total normality of solution adjusted on 0.01. As it is observed from the curves both zeolites have good selectivity toward uranyl ion against the sodium.

In order to optimize the design of an adsorption system to remove uranium(VI) from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curves.

The Langmuir and Dubinin-Radushkevich models are often used to describe equilibrium adsorption isotherms. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into the adsorption mechanisms, the surface properties and affinities of the sorbent.

The most widely used isotherm equation for modeling equilibrium data is the Langmuir model. The model is based on the assumption that maximum adsorption corresponds to saturated monolayer of uranium(VI) molecules on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate in the zeolite surface as shown in Figs. 6-9, the plots confirmed that the adsorption equilibrium data fitted very well to the Langmuir model in the studied conditions.

Plots of $\ln K_c$ vs. A_z were constructed using Kielland program in Matlab software [11]. This program calculates corrected and adjusted ionic activity coefficients in the solid and liquid phases. Extrapolations to $A_z=1$ were used to have a more accurate integralization of the kielland diagram that leads to calculation of the activity coefficients in zeolite phase. Representative Kielland plots of $UO_2/Na-A$ and $UO_2/Na-P$ systems at 25.0 °C and 50.0 °C were non-linear; this behavior was a consequence of different sets of exchange sites in zeolite.

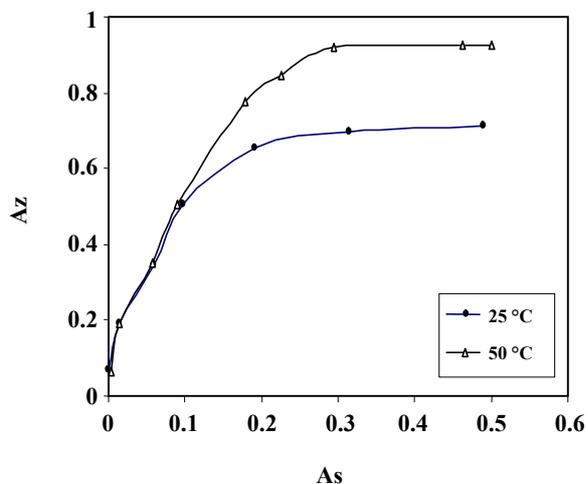


Fig. 4: Ion exchange isotherm of zeolite A.

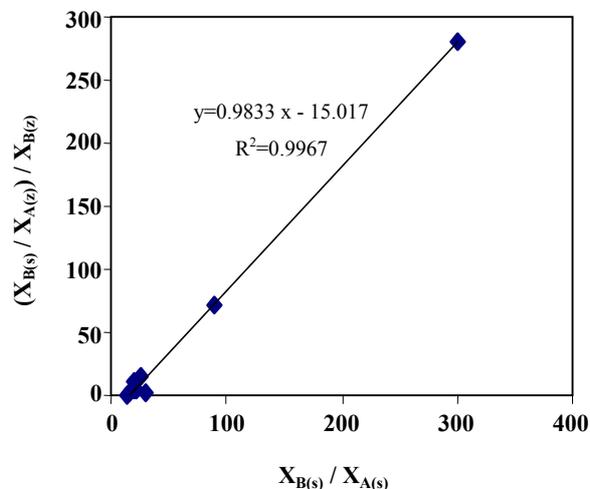


Fig. 7: Langmuir isotherm for zeolite A at 50 °C.

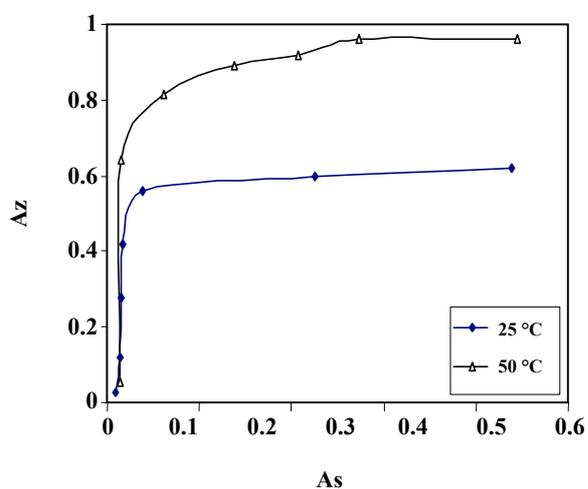


Fig. 5: Ion exchange isotherm of zeolite P.

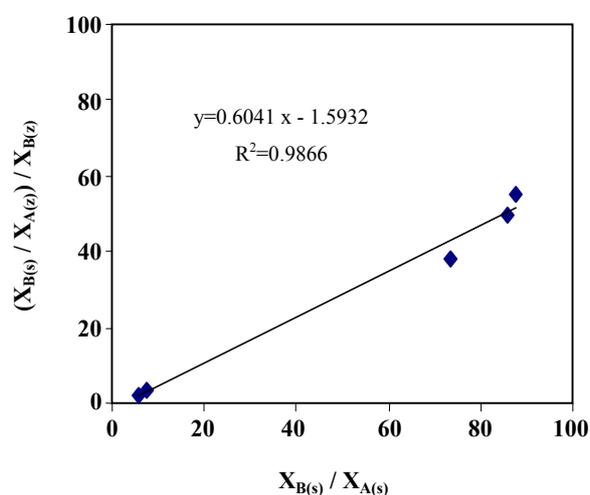


Fig. 8: Langmuir isotherm for zeolite P at 25 °C.

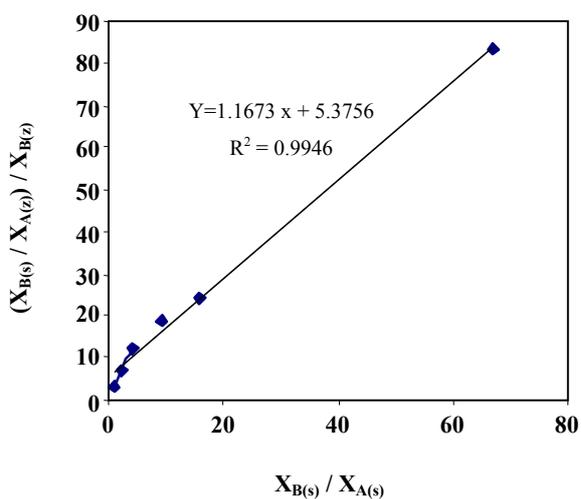


Fig. 6: Langmuir Isotherm for zeolite A at 25 °C.

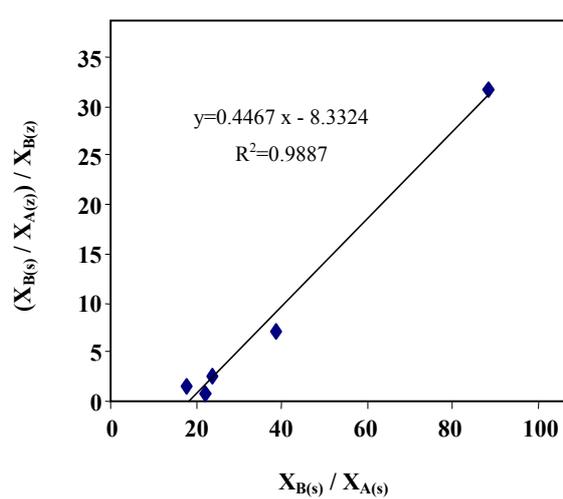


Fig. 9: Langmuir isotherm for zeolite P at 50 °C.

Table 1: Thermodynamic data for zeolite A.

Temperature	ΔG° (kJ/mol)	ΔH° (J/mol)	ΔS° (J/mol)
25 °C	-0.6779	40.84	2.41
50 °C	-0.6988	40.84	5.39

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG° , is the fundamental criterion of spontaneity. Thermodynamic parameters such as enthalpy (ΔH°), the Gibbs free energy (ΔG°) and entropy (ΔS°) for using uranium(VI) adsorption by zeolites were calculated using the following equations:

$$\Delta G^\circ = \frac{RT}{z_A z_B} \ln K_a \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (12)$$

R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is absolute temperature in Kelvin. Results are shown in tables 1 and 2.

The negative value of ΔG° is due to the fact that the adsorption process is spontaneous with affinity of uranium(VI) to zeolites. However, the negative value of ΔG° increased with an increase in temperature, indicating that the spontaneous nature of exchange of uranium(VI) is proportional to the temperature. Positive values of ΔH° suggests the endothermic nature of the exchange of uranium(VI) on zeolites. The positive value of ΔS° reflected the affinity of the zeolites for uranium(VI) and confirms the increased randomness at the solid solution interface during ion exchange.

CONCLUSIONS

In this study, zeolites were synthesized and the adsorption properties for uranium (VI) by them was investigated. This study also clearly established that the zeolites are effective adsorbent for uranium (VI) removal from aqueous solutions. The uranium (VI) binding capacity by zeolites were strongly dependent on the initial uranium (VI) concentration and temperature. It was noted that an increase in the temperature resulted in a higher metal loading. The experimental results were analyzed using the Langmuir and Dubinin-Radushkevich isotherm models. Adsorption capacity increased slightly

Table 2: Thermodynamic data for zeolite P.

Temperature	ΔG° (kJ/mol)	ΔH° (J/mol)	ΔS° (J/mol)
25 °C	-0.3552	120.57	1.60
50 °C	-3.3694	120.57	10.81

with increasing temperature. Various thermodynamic parameters, such as ΔG° , ΔH° and ΔS° , were calculated from the data. The thermodynamics of uranium(VI) ion/zeolites system indicated spontaneous and endothermic nature of the process.

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