

KINETIC STUDIES OF URANIUM(VI) ADSORPTION ON A COMPOSITE  
ION EXCHANGER

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Received 17 June 1996

Accepted 1 July 1996

In this paper, we studied the continuous adsorption of uranium on a composite ion exchanger. The experimental study was carried out at optimum conditions of uranium uptake found in the previous study. For these conditions first the adsorption isotherm was determined. This isotherm shows non-linear sorption according to the Langmuir model. Then we investigated uranium adsorption at different time intervals at temperatures of 30 °C and 60 °C, respectively.

INTRODUCTION

Inorganic ion exchangers are sparingly soluble compounds capable of exchanging cations or anions from the solution under contact with the exchanger. When compared with synthetic organic ion exchangers, they exhibit a broad variety of advantageous properties, e.g. higher thermal and radiation stability, often good chemical stability even in strongly acidic media, quick ion exchange kinetics and high selectivities for the capture of

certain ions. But on the other hand, their unsuitable granulometric and mechanical properties limit their use in column applications.

The preparation method of composite ion exchangers can be applied for most of the inorganic ion exchangers known. There is virtually universal accord in the scientific community that sorption processes play an important role in the transport and disposition of organic contaminants in subsurface systems. Moreover, composite ion exchangers have been developed for selective separation and concentration of radionuclides from environmental samples and for the removal of these radionuclides from liquid radioactive wastes<sup>1,2</sup>.

Recently zeolite matrix composites (C-X) have generated considerable interest in the materials field because of their attractive physical and mechanical properties.

Langmuir (1926) has described the role of solid surfaces in chemical reactions. He proposed that the molecules were bonded to the catalyst surface chemically. This is known as chemisorption. This phenomenon is different from physical adsorption in that the molecules are attracted to the solid surface by Van der Waals forces<sup>3</sup>.

Several conceptual and empirical models have been used to describe the equilibrium phase distribution for the sorption of uranium in surface systems. Although the Langmuir model was originally developed to describe the adsorption of gases, the equation may be written in the following form for solid-liquid systems:

$$C/y = (1/a) + (b/a) \cdot C \quad (1)$$

where C is the concentration of solute in the solution phase at equilibrium (g/l), y is the amount of solute

sorbed per unit weight of sorbent (mg/g),  $b$  and  $a$  are the Langmuir constants;  $b$  is represented as the ratio of adsorption and desorption rate coefficients (l/g), and

$$a = b \cdot Q^\circ \quad (2)$$

$Q^\circ$  is the maximum sorption capacity (mg/g). At low concentrations the Langmuir equation reduces to a linear relationship, while the maximum sorption capacity,  $Q^\circ$ , 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.

The following assumptions are implicit in the kinetic derivation of the Langmuir equation: (a) adsorption is site-specific or localized with no interactions between adsorbed molecules; (b) the energy of adsorption is constant for all sites; and (c) adsorption is limited to monolayer coverage. While these assumptions are rarely met in environmental systems, the form of the Langmuir model still has practical utility as a means for characterizing empirical sorption data that exhibit a limiting sorption capacity. The model has been used, for example, to describe the sorption behavior of such substances as heavy metals and surfactants<sup>4</sup>. Most environmental sorption processes are less energetically straightforward than those suggested by either the linear free energy partitioning model or the constant-energy limited-surface Langmuir model<sup>5</sup>.

Kitchener (1965) has given a good introductory account of the conditions under which one can expect to draw meaningful conclusions from the shape of the adsorption isotherm<sup>6</sup>.

In this study kinetic data were not expressed as the distribution coefficient  $K_d$  vs. time curves, because  $K_d$

vs. time curves reflect not only differences in kinetic, but also large differences in equilibrium chemistry. It is necessary, therefore, to normalize the data in terms of fractional attainment of equilibrium. Chiarizia et al. (1994) reported rate data in terms of fractional attainment of the equilibrium and derived a simplified rate equation<sup>7</sup>. The fractional attainment of equilibrium, defined as

$$F = \frac{[\bar{M}]_t}{[\bar{M}]_{eq}} \quad (3)$$

where the bar represents the composite ion exchanger phase,  $(\bar{M})_t$  and  $(\bar{M})_{eq}$  is a metal cation (charges are omitted for simplicity). Then the rate equation was obtained as

$$\ln (1-F) = -kt \quad (4)$$

where  $k(\text{min}^{-1})$  is the experimentally observed overall rate constant.

On the other hand, when diffusion inside the particles of ion exchanger is the rate-controlling process, for the limiting case of isotope exchange, a more complicated rate law is reported<sup>7</sup>. For practical purposes, Vermeulen's approximation, valid in the whole range of F, can be used:

$$\ln (1-F^2) \cong -kt \quad (5)$$

where, the constant k has the following meaning

$$k \propto (D/r_0^2) \quad (6)$$

D is the diffusion coefficient and  $r_0$  is the radius of the composite ion exchanger disks.

In this study, the adsorption kinetics of U(VI) ions in aqueous solution on a composite ion exchanger based on zeolite X was investigated at various temperatures and initial concentrations using above equations.

## EXPERIMENTAL

### Reagents

All chemicals used for the synthesis of the composite ion exchanger were of analytical reagent grade. Aqueous reagents were prepared in deionized-distilled water. The standard uranium solution was prepared by dissolving analytical grade Merck  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  salt, adding some drops of concentrated nitric acid.

### Materials and methods

The composite ion exchanger has been prepared from an inorganic ion exchanger as the active component and polyacrylonitrile (PAN) as the binding polymer. Very fine colloidal particles of zeolite X used as the active component were treated with a solution of the binding polymer. The final product was shaped as a very thin film, washed with distilled water and dried at room temperature. In further experiments, the fraction with the size (0.05 - 0.075 x 0.55 $\phi$ ) mm was used<sup>8</sup>.

The composite ion exchanger (0.05 g) and 54 - 1890  $\mu\text{g}$  U/ml  $\text{UO}_2(\text{NO}_3)_2$  aqueous solution were shaken for 24 h at 30 °C for determining the Langmuir isotherm. The composite ion exchanger (0.05 g) was suspended in 50 ml of solution (pH 5) containing 2.5 - 50 mg of uranium. The pH of the solution was adjusted to the desired value with 0.1 - 0.01 mol/l  $\text{NaHCO}_3$  or 0.1 mol/l  $\text{HNO}_3$  solution. The suspension was stirred continuously for different time intervals at 30 and 60 °C, respectively.

Continuous kinetic experiments, where the rate of uranium uptake was followed on the same solution using a single test for the whole kinetic curve. The advantage of this technique is that the whole kinetic experiment

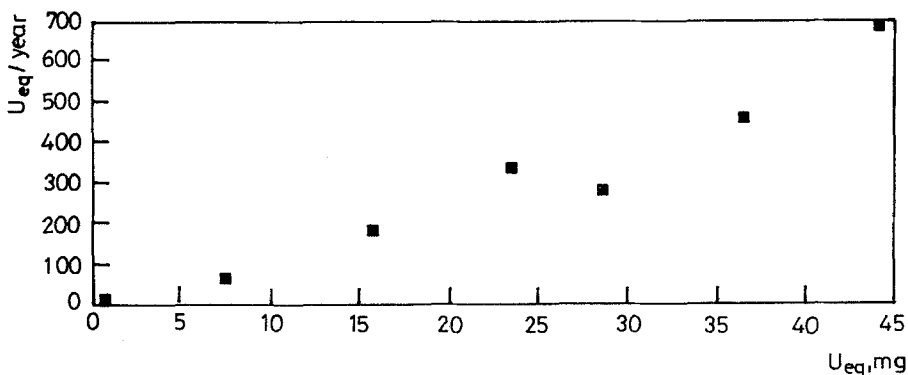


Fig. 1. Langmuir isotherm;  $a = 0.1055$ ,  $b = 0.6957$  l/g,  $Q^\circ = 0.1517$  mg/g and  $r = 0.98$

was followed in a solution-composite-ion-exchanger system having a constant composition.

The volume of the aqueous solution taken with a calibrated automatic pipette, was between 50 and 100  $\mu$ l. The  $UO_2^{2+}$  concentration in the solution was determined spectrophotometrically with Arsenazo III ( $\epsilon = 1.27 \times 10^5$  l.mol<sup>-1</sup>.cm<sup>-1</sup>,  $\lambda = 665$  nm)<sup>9</sup>.

## RESULTS AND DISCUSSION

Sorption data were expressed as the amount of uranium sorbed per unit weight of sorbent ( $U_{eq}/y$ ) versus the concentration of uranium in the solution phase at equilibrium ( $U_{eq}$ ). These data conformed to Langmuir's Eq. (1). The sorption data were fitted to the non-linear form of Eq.

(1) to obtain the values of  $a$ ,  $b$  and  $Q^\circ$  shown in Fig. 1<sup>10</sup>

Figures 2 and 3 show similar kinetic data for uranium (VI), sorbed at 30 and 60 °C. Also in this case the data show a higher uptake of U(VI) ion by the composite ion exchanger. The effect of the chemical nature of U(VI) in

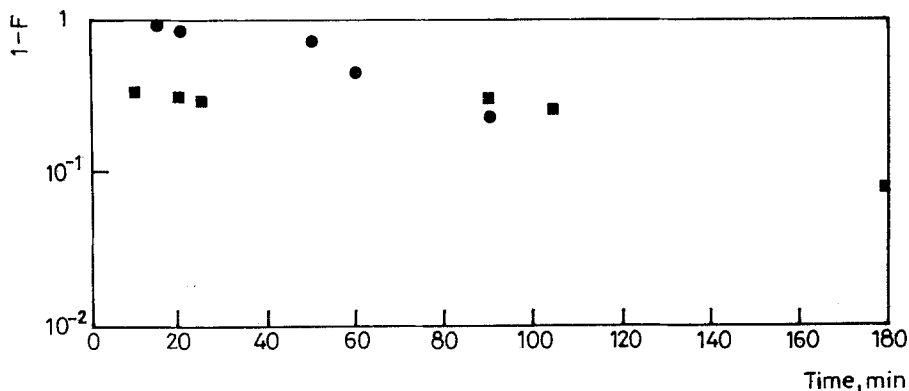


Fig. 2. Fractional attainment of equilibrium for U(VI) uptake from aqueous solution at different temperatures and pH 5 for 50 µg U/ml (●, 30 °C; ■, 60 °C)

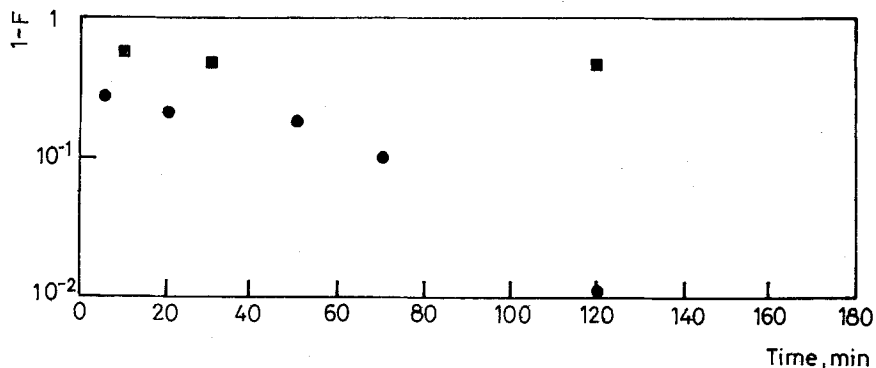


Fig. 3. Fractional attainment of equilibrium for U(VI) uptake from aqueous solution at different temperatures and pH 5 for 250 µg U/ml (●, 30 °C; ■, 60 °C)

solution on the uptake rate of uranium ions is complicated and can only be explained in part. However, the kinetic curves follow, at least qualitatively, the behavior of the system predicted for film-diffusion control.

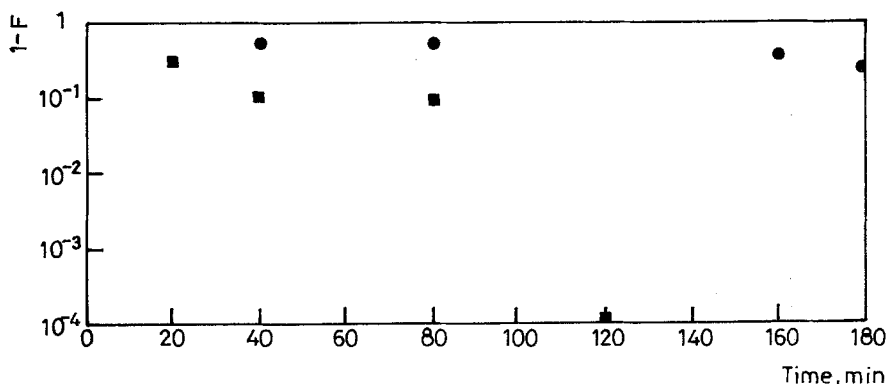


Fig. 4. Fractional attainment of equilibrium for U(VI) uptake from aqueous solution at 30 °C and pH 5 for 750 (■) and 1000 µg U/ml (●)

The rate constant of the reaction ( $k$ ) was calculated from Eq. (4) as  $9.21 \times 10^{-3} \text{ min}^{-1}$  and  $1.29 \times 10^{-3} \text{ min}^{-1}$  for 50 µg U/ml for 30 and 60 °C, respectively. Ratio of the diffusion coefficient in composite ion exchanger at two different temperatures  $D_{30}/D_{60}$  was calculated as 7.14 (Fig. 2).

For 250 µg U/ml, the rate constant ( $k$ ) was calculated from Eq. (4) as  $2.21 \times 10^{-3} \text{ min}^{-1}$  and  $7.28 \times 10^{-4} \text{ min}^{-1}$  for 30 and 60 °C, respectively (Fig. 3). While the initial uranium concentration in the solution was increased from 50 to 250 µg U/ml, the ratio of diffusion coefficients in the composite ion exchanger at two different temperatures ( $D_{30}/D_{60}$ ) decreased from 7.14 to 3.04.

It was observed that a significant amount of U(VI) precipitated at 750 and 1000 µg U/ml concentrations when the temperature of solution was adjusted to 60 °C. For this reason, only at 30 °C was the study carried out. The results are shown in Fig. 4. Rate constant of reaction ( $k$ ) was calculated from Eq. (4) as  $2.63 \times 10^{-3} \text{ min}^{-1}$  and  $1.80 \times 10^{-3} \text{ min}^{-1}$  for 750 and 1000 µg U/ml for 30 °C, respectively.



## CONCLUSIONS

In the present work we report kinetic studies on the uptake of uranium by a composite ion exchanger at different time intervals and at 30 and 60 °C temperatures. The results obtained allow the following conclusions:

- The maximum sorption capacity was calculated as 0.1517 mg/g composite ion exchanger, and the reaction follows a non-linear form of the Langmuir model.
- The incremental increase in the amount of uranium adsorbed in the composite ion exchanger is rather difficult to treat theoretically. It appears that only a relatively thin layer is formed and further additions are strongly opposed by the solvating power of the solvent<sup>11</sup>.
- At 50 µg U/ml at 60 °C the reaction reached 43.3% in about 90 min. The reaction was complete with 19.14% in 90 min at 30 °C. At 250 µg U/ml concentration at 60 °C the reaction is still relatively slow, with 29.5% completion being reached in about 120 min. However, the reaction was complete with 60.9% at 120 min at 30 °C.
- At 750 µg U/ml concentration at 30 °C the reaction reached 14.7% in 120 min. At 1000 µg U/ml concentration at 30 °C, the reaction reached 24.1% in 180 min.
- It is concluded that the percent uptake is decreased with increasing temperature at high concentrations of uranium.

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