Kinetics of uranium sorption from acidic sulphate solutions onto crosslinked polyethyleneimine based resins. 10

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SUMMARY

The kinetics of uranium sorption at very low solution concentration onto hydrophilic crosslinked polyethyleneimine based resin have been studied by the finite solution volume method. The shrinking core model of Gopala and Gupta was used for testing film or particle diffusion rate control. Particle diffusion of the low—concentration mechanism to control the rate of uranium sorption was found.

INTRODUCTION

The emergence of several new continuous ion exchange techniques capable of treating uranium ore pulps and unclarified liquors has brought a revival of interest in the development of ion exchange materials due to the current interest in uranium recovery (1). On that account, we have prepared and studied different ion—exchange resins prepared by crosslinking poly-ethyleneimine (branched or linear) with several dihalogenated derivatives, and have reported that some of them would be useful for the removal and recovery of heavy metals, like uranium, because of their high adsorption capacity and selectivity (2—8). However, the efficient design of continuous processes requires considerable knowledge of the relevant stages in the ion exchange reaction, especially information on the rate of up—take of the ionic species from aqueous solutions. The work on uranium extraction is extensive but there are surprisingly little systematic data on the kinetics of uranium extraction and elution from anionic exchange resins.

Recently, Gopala and Gupta have developed quantitative rate laws, based on Levenspiel's shrinking—core mathematical model, which have been useful for testing film or diffusion rate control (9). Thus, this report concerns with the kinetics of uranium sorption onto a resin obtained by crosslinking branched polyethyleneimine with 1—chloro—2,3—epoxypropane (10) at very low solution concentrations by using the finite solution volume method (11), and the use of the above mentioned rate laws to provide a rational basis for a further perspective in using this resin for uranium recovery from copper ore leaches.

EXPERIMENTAL

Resin was obtained as usual by crosslinking branched polyethyleneimine with 1-chloro-2,3-epoxypropane (10). Conditioned resin samples in the chloride form were used in the experiments. The resin particles were sized by wet screening and narrow cuts of (-40 +60) and (-60 +120) mesh size were used. Diameters of the fully-swollen wet resin beads were mesured with a calibrated microscope. Anion exchange capacity (12) and dryness fraction (13) (oven dry) of the resin were also determined.

The finite solution volume method was used in the present study keeping the following constants conditions:

Dry resin weight   : $W=2.0$ g

Initial solution volume   : $V=2000$ ml

Initial uranium concentration : $C = 10$ mg/l

Solution pH   : 2.0

Particle size and stirring speed were varied; the solution was stirred at the selected stirring speeds and the dry equivalent weight of the drained resin was added at the start of the run. Then 25 ml of resin-free liquid samples, at desired time intervals, were withdrawn and analyzed for uranyl ions by a spectrophotometric method (14). All the experimental runs were made at room temperature (15 to 18°C).

By means of graphical integration from a plot of solution concentration C_b, vs. time, t, values of $\int_0^t C_b dt$ at desired values of t were obtained. From the primary experimental data, fractional attainment of equilibrium, X at considered values of time were calculated.

RESULTS AND DISCUSSION

The crosslinked polyethyleneimine resin possesses secondary and tertiary amine groups which form adducts with the uranyl sulphate (1). This resin in free-base form shows a low degree of crosslinking (12%) and N-alkylation (44%) which were determined by elemental analysis considering the C/N mol ratio and chlorine content. Furthermore, the resin shows a water content of 72% which indicates a high pore volume. The average diameters for (-40+60) and (-60+120) mesh size of fully-swollen wet resin bead samples in the chloride form were 0.043 and 0.023 cm, respectively. Anion exchange capacity for both particle sizes was found to be 7.4 meq/g of oven dry resin, or 1.8 meq/ml of swollen solid bead volume, within experimental error.

To study the kinetics of uranium sorption from acidic sulphate solution onto the above resin four different essays at the various experimental conditions were performed, as shown in Table 1.

Table 1. Variable experimental conditions

Essay	E1	E2	E3	E4
Stirring Speed (rpm)	400	700	400	700
Average Diameter (cm)	0.043	0.043	0.023	0.023

      Figure 1 shows the fractional attainment of equilibrium (X) as a function of time for the uranium sorption on the chloride form of resin at two different particle sizes and stirring speeds. These preliminary results indicate that the stirring speed had no or little effect on the sorption rate. In contrast, smaller particle size enhanced the sorption rate with fractional attainment higher than 80% in less than 15 minutes.
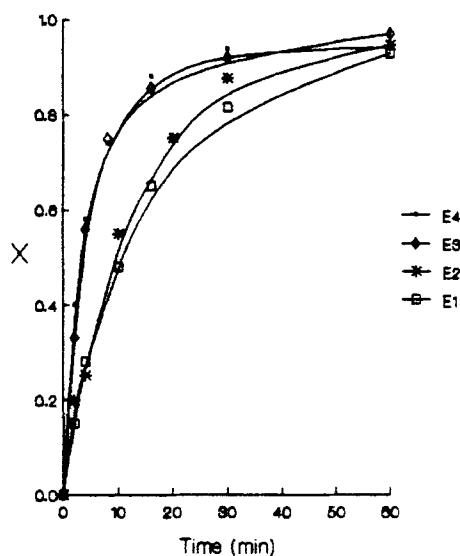

Figure 1. Particle size and stirring effect on the kinetics of uranium sorption.

      The kinetic data was tested for film or particle diffusion rate control using the shrinking core model of Gopala and Gupta (9).

      For film-diffusion control, the fractional attainment of equilibrium, X is given by:

$$X(t) = \frac{3Df}{CaR\delta} \int_{0}^{t} Cbdt$$

where Cb and Ca are the initial uranium concentration in the solution (meq/ml) and the anion exchange capacity of the resin (meq/ml), respectively, R is the radius of the particle (cm), δ is the effective film thickness (cm) and Df is the effective diffusion coefficient in the liquid film (cm^2/s).

For pore—diffusion control, a function of X is given by the following equation:

$$F(X) = [1 - 3(1-X)^{2/3} + 2(1-X)] = \frac{6Dp}{CaTR^2} \int_0^t Cbdt$$

where symbols are as before except Dp which is the effective diffusion co-efficient in the resin phase (cm^2/s).

The uranium sorption data was best correlated by the pore—diffusion controlled shrinking—core model as shown in Figure 2.
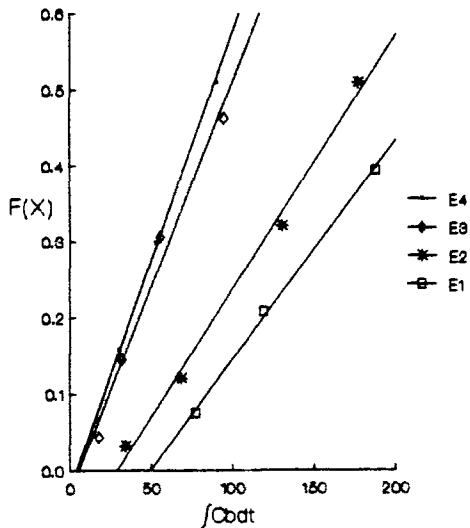

Figure 2. Correlation of kinetic data of uranium sorption: Pore—diffusion shrinking—core model.

The straight-lines did not pass through the origin, possibly because the initial part of the exchange rates were controlled by film—diffusion.

Effective diffusion coefficients were calculated from the slopes of the straight-lines showed in Figure 2 and are summarized in Table 2.

Table 2. Effective diffusion coefficients Dp

Essay	E1	E2	E3	E4
Dp x 10^7 (cm^2/s)	3.84	4.27	2.91	2.66

These results are in agreement with earlier experimental observations by other authors which show that the ion exchange reactions involving uranyl sulphate species and weak base resins are predominantely particle diffusion controlled (1).

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