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Kinetics of uranium sorption from acidic sulphate solutions onto crosslinked polyethyleneimine based resins. 11

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SUMMARY

The kinetics of uranium sorption from acidic sulphate solutions onto weak base resins derived from branched polyethyleneimine have been studied. Finite solution volume method and shrinking core model of Gopala and Gupta for testing film or pore diffusion rate control were used. Remarkably pore diffusion was the rate controlling mechanism for the smaller particle size considered. Stirring rate was found to be negligible on uranium sorption.

INTRODUCTION

Hydrometallurgical recovery of uranium from sulphuric acid leached mineral ore-bodies by ion exchange materials is widely known (1). However, several new continuous ion exchange techniques have been developed due to the current interest in uranium recovery, so that a renovable interest in the development of ion exchange materials has brought. On that account, we have reported earlier the synthesis and analytical properties of different weak base resins derived from branched or linear polyethyleneimines. Some of them have been shown to be potentially useful for removal and recovery of heavy metals, like uranium, because of their high adsorption capacity and selectivity (2-8).

Despite the vast amount of work on uranium extraction, there are little systematic data on the kinetics of uranium sorption whose knowledge and its prediction, for optimum design purposes, are essential. Thus we have chosen some of the best above mentioned resins such as those obtained from branched polyethyleneimine by crosslinkig with 1,3-dibromopropane, 1,2-dibromoethane and 1,4-bis(bromomethyl)benzene (9), to establish which is the rate controlling mechanism by the hand of finite solution volume method (10) and shrinking core model of Gopala and Gupta (11) for testing film or pore diffusion control because of our interest for a further perspective in using these resins for uranium recovery from copper ore leaches.

EXPERIMENTAL

Resins were synthesized, by crosslinking the branched polyethyleneimine with different dihalogenated derivatives such as: 1,3-dibromopropane (IM-BP), 1,2-dibromoethane (IM-BE) and 1,4-bis(bromomethyl)benzene (IM-BB) (9). The resins were conditioned by treating with 1 M HCl using the batch method. The chloride form of the resins were washed thoroughly with deionized water and were used in all the experiments. The resin particles were sized by wet screening, and cuts of (-40+60) and (-60+80) mesh sizes were used. Average particle diameter was determined with a microscope fitted with a calibrated occular eye piece. Anion exchange capacity (12) and dry fraction (oven dry) (13) were also determined.

The finite solution volume method (10) was used under the following constant 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 rate were the variables. The solution was stirred at the select stirring rate 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 were withdrawn, at the desired time intervals, and analyzed for uranyl ions by a spectrophotometric method (14). All the experimental runs were made in the range 15 to 18°C.

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

RESULTS AND DISCUSSION

The crosslinked polyethyleneimine resins contain secondary and tertiary amine groups able to form adducts with uranyl sulphate (1). The water content of the resins was in the range 68 to 76%, which indicates a high pore volume. The anion exchange capacity for both particle sizes are summarized in Table 1.

Table 1. Symbols of the resins according to the crosslinking agents used and anion exchange capacity.

CROSSLINKING AGENT	RESIN SYMBOL	ANION EXCHANGE CAPACITY(meq/ml) MESH SIZE (-40+60)	(-60+80)
1,3-dibromopropane	IM-BP	1.8	1.5
1,2-dibromoethane	IM-BE	1.9	1.5
1,4-bis(bromomethyl)benzene	IM-BB	1.3	1.0

Different essays were performed to study the kinetics of uranium sorption from acidic sulphate solution onto the above polyethyleneimine based resins . The experimental conditions used as well as average diameter, for (-40+60) and (-60+80) mesh size of fully-swollen wet resin beads and stirring rate are shown in Table 2. A comercial resin, IRA-400, is included for comparison.

Table 2. Experimental conditions

Essay	Resin	Average Diameter (cm)	Stirring Rate (rpm)
E11	IM-BP	0.028	400
E12	"	0.028	700
E13	"	0.019	400
E14	"	0.019	700
E21	IM-BE	0.037	400
E22	"	0.037	700
E23	"	0.022	400
E24	"	0.022	700
E31	IM-BB	0.035	400
E32	"	0.035	700
E33	"	0.021	400
E34	"	0.021	700
IRA-400		0.047	400

Figure 1 shows the fractional attainment of equilibrium (X) as a function of time for uranium sorption of IM-BE at the two different particle sizes and stirring rates. Similar results were also obtained for resins IM-BP and IM-BB . These preliminary results indicate that the stirring rate had a negligible effect on the sorption rate. On the other hand, smaller particle size enhanced the sorption rate remarkably with fractional attainment higher than 80% before 25 minutes.

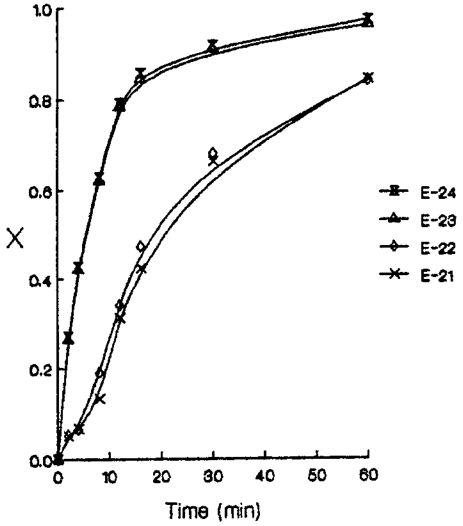

Figure 1. Particle size and stirring rate effect on the kinetics of uranium sorption with IM-BE.

Therefore, the kinetic data was testing for film or particle diffusion rate control using the shrinking core model of Gopala and Gupta (11). Thus, for film-diffusion control:

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

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:

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

where the symbols are as before except Dp is the effective diffusion coefficient 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 for essays performed at 400 rpm and the smaller particle size of each resin.

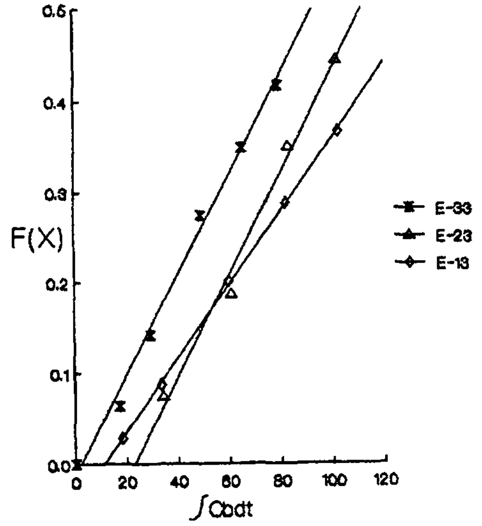

Figure 2. Correlation of kinetic data of uranium sorption: Pore-diffusion shrinking-core model (400 RPM, -60/+80 mesh size).

Even so, the straight-lines did not pass through the origin, because it is possible that the initial part of the exchange rates were controlled by film-diffusion even though the whole data did not correlate well (Figure 3.).

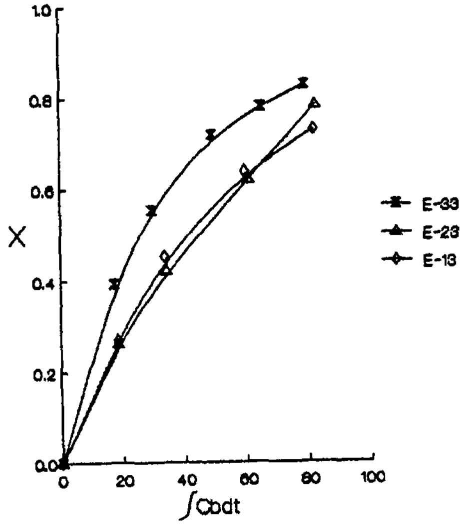

Figure 3. Correlation of kinetic data of uranium sorption: Film-diffusion shrinking-core model (400 RPM, -60/+80 mesh size).

As the particle size increased, slopes of the pore diffusion plots decreased, showing a disminished sorption rate relating to those performed with the smaller particle size (Figure 4).

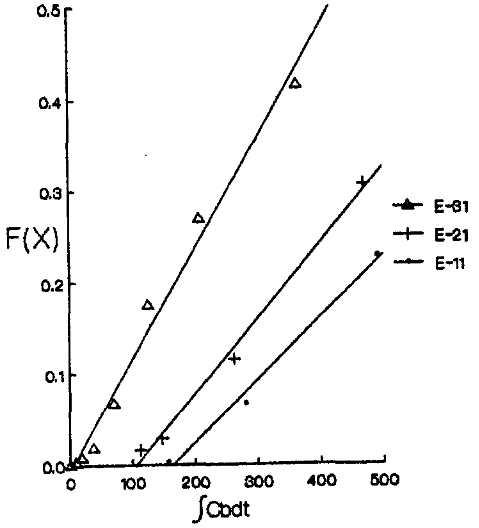

Figure 4. Correlation of kinetic data of uranium sorption: Pore-diffusion shrinking-core model (400 RPM, -40/+60 mesh size).

Effective diffusion coefficients were calculated from the slopes of the straight-lines shown in Figures 2 and 4. These data are summarized in Table 3.

Table 3. Effective diffusion coefficients Dp

Essay	Dp (cm^2/s)x10^7
E-11	0.65
E-13	0.90
E-21	1.30
E-23	1.64
E-31	0.67
E-33	1.02
IRA-400	1.85

The effective pore-diffusion coefficients for uranyl sulphate were in range from 0.65 to 1.64x10^{7}cm^2/s for polyethyleneimine-based resins, so that with the smallest particle size were greater than the largest ones. These results show that IRA-400 has a larger effective pore-diffusion coefficient than the resins examined.

CONCLUSIONS

These results are in agreement with earlier experimental observations by other authors showing that the ion exhange reactions involving uranyl sulphate and weak base resins are predominantely particle diffusion controlled (1). In contrast, effective diffusion coefficients shown by the resins studied were lower than that of IRA-400 under the same experimental conditions. Stirring rate does not affect the uranium sorption rate.

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REFERENCES

1. C.D.Barnes, R.A. da Silva and M.Streat, J.Appl.Chem.Biothecnol. 24, 787 (1974).
2. B.L.Rivas, H.A.Maturana, I.M.Perich and U.Angne. Polym.Bull. 14, 239(1985).
3. B.L.Rivas, H.A.Maturana, I.M.Perich and U.Angne. Polym.Bull. 15, 121 (1985).
4. B.L.Rivas, H.A.Maturana, J.Bartulín, R.E.Catalán, and I.M.Perich. Polym.Bull. 16, 299 (1986).
5. B.L.Rivas, H.A.Maturana, U.Angne, R.E.Catalán and I.M.Perich. Polym.Bull.16, 305 (1986).
6. B.L.Rivas, H.A.Maturana, U.Angne, R.E.Catalán and I.M.Perich. Eur.Polym.J. 24, 967 (1988).
7. B.L.Rivas, H.A.Maturana, R.E.Catalán, I.M.Perich and U.Angne. Polym.Bull.19, 609 (1988).
8. B.L.Rivas, H.A.Maturana, R.E.Catalán, I.M.Perich. Bol.Soc.Chil.Quím. 33, 151 (1988).
9. J.Bartulín, H.A.Maturana, R.E.Catalán, I.M.Perich. Bol.Soc.Chil.Quím. 29. 373 (1984).
10. Y.Sano, N.Yamaguchi, J.Adachi, J.Chem.Eng.Japan 7, 255 (1974).
11. M.Gopala, A.K.Gupta. AICH Symposium Series 78, N°219, 103 (1982).
12. R.Kunin, "Ion Exchange Resins" Jhon Wiley & Sons, 2d.Ed., pg. 345 (1958).
13. American Society for testing materials. A.S.T.M. Standards 31, 834 (1974)
14. J.A.Pérez, F.Palomares. Analyst 96, 407 (1971).

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