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A Kinetic Investigation of Chromium

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Abstract. A kinetic investigation was performed with an ion exchange resin for chromium. A chelating cation exchange resin (Amberlite IRC 718) was used for removal and recovery of chromium. The effect of concentration, resin amount, particle size and stirring speed on kinetics were investigated. The metal concentration range studied was between 5 to 160 mg L^{-1}, the resin amount range was between 5 to 20 mg, the particle size range was between 0.35 to 1.8 mm and the stirring speed range was between 1000 to 3500 rpm.

Kinetic studies were done using a Kressman-Kitchener stirrer reactor system and the results were compared with existing kinetic models. Two models; Nernst-Plank film diffusion control model (fdc) and solid phase diffusion control model (pdc) were identified and the dependence of the rate on parameters, such as solution concentration, particle size, resin amount, stirring speed, etc., was examined for each of them. As a result, interpretation of these data showed that the system is probably controlled both film and particle diffusion.

Keywords: kinetics, chelating weakly acidic exchange resin, chromium, Kressman-Kitchener stirrer reactor

1. Introduction

The kinetics of liquid-solid ion exchange reactions has been widely studied in recent years. Ion exchange may be considered a statistical redistribution of ions between the exchanger and the contracting liquid phase, with rates usually controlled by the resistance to mass transfer in the solid or the liquid phase or both (Petruzzelli et al., 1987). Accordingly, ion exchange kinetics has been described in terms of Fick's laws, with rates depending on the ion concentration gradients in the respective medium. This aspect of ion exchange has been considered from both theoretical and experimental points of view, and several different rate equations have been proposed. Recent studies have shown that mass transfer phenomena, either in the liquid and/or the solid phase, could play a relevant role in determining general kinetic behaviour of these systems in addition to those strictly related to the pure chemical reactions (Petruzzelli et al., 1991; Phelps and Ruthven, 2001; Karpov et al., 2001; Beleza et al., 2001). The chemical exchange on the fixed charge is usually assumed too fast to affect the overall exchange rate, unless chemical modifications occur during exchange (Boyd et al., 1947).

Chelating cation exchangers appear to be very promising for full scale applications in water conditioning (demineralisation, softening) wastewater treatment for pollutant control and recovery. The kinetic performances of these exchangers appear to be faster than other traditional ion exchange resins (Petruzzelli et al., 1996; Kocaoba and Akcin, 1999; Koivula et al., 2000; Kocaoba and Akcin, 2002).

A large number of practical applications of ion exchange to environmental protection involve multicomponent systems and most importantly, specific interactions in the solid phase between the mobile species and the fixed groups.

In this study, a kinetic investigation was performed with a chelating cation exchange resin (Amberlite

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IRC 718) for chromium and kinetic data were evaluated for Nernst-Plank film diffusion control and solid phase diffusion control models.

1.1. Theory

Nernst-Plank Film Diffusion Control (fdc) Model. In this model, the slow and sole rate controlling step is mass transfer in the liquid phase. In terms of the Nernst film concept, the flux equation for this model is

$$J = D\Delta C/\delta \tag{1}$$

When Eq. (1) integrated, yields

$$\ln(1-U)+(1-\alpha_{\mathrm{BA}})U = -3DC\,\alpha_{\mathrm{BA}}t/r^{\mathrm{o}}\delta\bar{C} \tag{2}$$

Of special interest in the present context is the limiting case with very large value of the separation factor α_{BA}, corresponding to the uptake of a highly preferred counterion. For $\alpha_{\mathrm{BA}} \geq 1$ and not too small values of $1-U$, the left side of Eq. (2) is dominated by the second term and the equation reduces to:

$$U \approx 3DCt/r^{\mathrm{o}}\delta\bar{C} \tag{3}$$

This reflects a linear dependence of fractional conversion on time, i.e., a constant rate of exchange (Helfferich et al., 1985a). The reference physical model assumes that overall exchange phenomena are controlled by the liquid-phase mass transfer resistance to ionic interdiffusion in the stationary liquid film around the exchanger particle, on the basis of the “Nernst film concept”. The model assumes the following as fundemantal premises: the exchanger phase containing ion A as the only counterion, in contact with the solution of constant concentration of counterion B; linear driving force for the ion concentration profiles through the stationary liquid film; constant separation factor, α_{BA}, for exchanging ions at a given solution concentration; no concentration gradients of ions and no uptake or release of water by the solid phase; quasi-stationary state of liquid phase mass transfer (Helfferich et al., 1985b). Of course, instead of Fick’s law the Nernst-Plank equations (Helfferich, 1966; Nernst, 1888, 1889; Plank, 1890), which include the effect of transference, can be integrated over the film. However, this amounts to taking the fictitious film at face value when calculating and evaluating non-linear concentration profiles in it, although the model is based on linear extrapolation. Clearly, this puts too much strain on the model. Not surprisingly, the film model usually gives only marginally better results than the very much simpler linear driving force approximation for the film.

Solid Phase Diffusion Control with Nernst-Planck Equations (pdc). In this model, the slow and sole rate-controlling step is diffusion within the exchanger particle. The model assumes or implies; no concentration gradients in the liquid phase, no convection (e.g., through solvent uptake or release) in the solid phase.

The model describes diffusion with the Nernst-Planck equations (Helfferich et al., 1985a)

$$J_i = -D_i[\mathrm{grad}\,C_i + z_iC_i(U/RT)\mathrm{grad}\,\varphi] \quad (i = A, B) \tag{4}$$

which account for electric potential gradient, grad φ, generated by ionic diffusion. For complete conversion and constant solution concentration, numerical solutions have been approximated by empirical equations. In this model, the selectivity (separation factor) does not directly affect the rate. An indirect effect of selectivity on rate is probable. It stands to reason that high selectivity arises at least in part from a strong attracting interaction between exchange groups and the preferred counterion. Such an interaction is likely to impede that ions mobility, i.e., reduce its intraparticle diffusivity. Time is required for any given conversion is proportional to the square of the particle radius and is independent of the solution concentration.

Table 1 are shown, the effects of experimental variables on the ion-exchange rate controlled by

Table 1. Dependence of ion-exchange rates on various experimental parameters.

Experimental parameter	Liquid-phase mass transfer (fdc)	Intraparticle diffusion (pdc)
Particle size (r^0)	Proportional to $1/r^0$	Proportional to $1/r^{02}$
Solution concentration (C)	Proportional to C	Independent
Stirring rate (rpm)	Sensitive	Independent
Exchanger capacity ($\bar{C}$)	Proportional to $1/\bar{C}$	Independent
Interruption test	Not sensitive	Sensitive

intra-particle diffusion, and by liquid-phase mass transfer.

Models 1 and 2 additionally assume that no reactions involving the exchanging ions or fixed groups occur.

1.2. Kressman-Kitchener Stirrer System

Kinetic determinations were made by means of a modification of Kressman-Kitchener stirrer reactor technique (Kressman and Kitchener, 1949; Helfferich et al., 1985b). In this system, rapid stirring of the solution (1000–3000 rpm) is essential to minimize mass transfer resistance related to ion diffusion through the liquid film surrounding the resin beads. Use of paddle or magnetic stirrers may produce severe cracking of the resin beads. An interesting solution is offered by the Kressman-Kitchener centrifugal stirrer, where the ion exchanger (~10 mg) is held in the central part of the stirrer. Centrifugal action forces the inner solution to leave the stirrer through the radial holes in the casing, being instantaneously replaced by fresh solution entering the cage at the bottom. Furthermore, it allows for almost instantaneous separation of ion exchanger and solution by raising the (still rotating) stirrer out of the solution (interruption tests). With this procedure the fractional attainment of equilibrium, U, can be directly evaluated by fitting experimental data (e.g., analysis of solution aliquots with drawn at various intervals) to proper equations (Liberti, 1983).

1.3. Interruption Tests

The interruption test is another method for determining the rate controlling mechanism (Helfferich et al., 1985b). To have more evidence on the controlling mechanism it is necessary to run interruption tests. By stopping the flow or removing the resin from the solution, sufficient time is given for the concentration gradients in both phases to relax. Because of particle diffusion is much slower than film diffusion, when the exchange process is resumed a relatively long period of time is required for a pre-interruption particle gradient to be re-established. As a result, the rate just after exchange begins is much higher than before the interruption if particle diffusion is controlling.

2. Materials and Methods

2.1. Ion Exchange Resin, Reagents, Solutions and Equipment

A weakly chelating cation exchange resin, Amberlite IRC 718 (Rohm and Haas Comp.) was used for the experiments. Its' physical properties reported by the suppliers are shown in Table 2. This resin was prepared in Na^+ form. Reagent grade basic chromic sulphate $[Cr_4(SO_4)_5(OH)_2]$ from Merck, Germany was used at different concentration levels. HCl, NaOH, NaCl were also used from Merck, Germany. Freshly prepared solutions were used throughout the experiments. Water was deionised and purified further with a Milli-Q water purification system (Millipore-USA). Kinetic determinations were performed by means of the Kressman-Kitchener stirrer reactor system as explained before. The initial and final chromium concentrations were determined by Atomic Absorption Spectrophotometry on a Model Spect. AA 20 from Varian.

2.2. Conditioning of the Resin

After three preliminary acid-base re-conversions of the resin with 1 M HCl and NaOH solutions to remove solvents and other preparation chemicals, the resin was finally converted to the sodium form using 1 M NaCl, and after sieved three different bead size, conditioned resin was dried under vacuum (40°C, 10 mm Hg) and stored in dry atmosphere.

2.3. Determination of the Resin Moisture Content

Accurately weighed samples of 1 g of ion exchange resin in Na^+ form were dried at 110°C, cooled in a desiccator and weighed. This was continued until the attainment of constant weight.

Table 2. The main physicochemical properties of the resin investigated.

Resin	Functional group	Bead size (mm)	Matrix	Moisture holding capacity	Total exchange capacity
Amberlite IRC 718	Iminodi-acetic	0.4–1.8	Macroporous styrene divinyl benzene	Na^+ form 64 to 70%	Na^+ form ≥ 1.0 eq L^{-1}

Table 3. Chromium exchange capacities and moisture contents of the resin.

Resin (Amberlite IRC 718)	Na^+ form	H^+ form
Capacity (eq L^{-1}) (column)	0.63	0.38
Moisture content (%)	57.20	79.87

2.4. Determination of Ion Exchange Capacity

The chromium exchange capacity was determined for sodium form of the resin by using a column technique. Accordingly, after loading the sample (3 g) into a glass column the resin was eluted with an excess quantity of 20 mg/L chromium(III) solution. The results are given in Table 3 together with the determined moisture content.

2.5. Batch Kinetic Experiments

Kinetic Experiments were run in triplicate by means of the Kressman-Kitchener stirrer reactor technique. With this technique, appropriate amounts of the ion exchanger and solution, of known initial composition, are placed in a thermostated vessel and vigorously agitated. The time dependence of a representative variable of the system (e.g., pH, concentration) in the liquid phase is continuously followed. A rapid flow of solution circulates around the resin beads to minimize polarization concentration effects. This technique allows for almost instantaneous separation of ion exchanger and solution by raising the (still rotating) stirrer out of the solution (interruption tests). With this procedure the fractional attainment of equilibrium, U, can be directly evaluated by fitting experimental data to proper equations. The chromium concentration range studied was between 5 to 160 mg L^{-1}, the resin amount range was between 5 to 20 mg, the particle size range was between 0.35 to 1.8 mm and the stirring speed range was between 1000 to 3500 rpm (pH 5). Rapid stirring of the solution is essential to minimize mass transfer resistance related to ion diffusion through the liquid film surrounding the resin beads. After re-hydration during a full night in a humidity box, a weighed amount of Na^+ form resin sample (about 10 mg) was loaded in the reactor which was immersed while rotating into the reaction batch containing 1 L of basic chromium sulphate solution (pH 5), at predetermined concentration (i.e., 5–160 mg L^{-1}). At pre-determined times, small amounts of solutions were taken from the system. After three hours all chromium solution samples were determined by means of atomic absorption spectrophotometry. Fractional attainment of equilibrium (U) versus time curves were plotted. Kinetic studies were done with system and the results were compared with existing kinetic models. Results are given in Figs. 1–4.

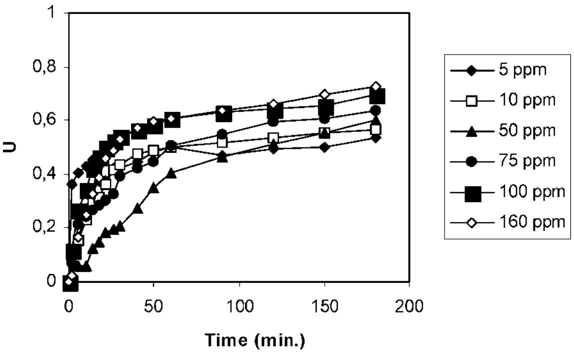

Figure 1. Concentration effect on retained chromium (pH 5).

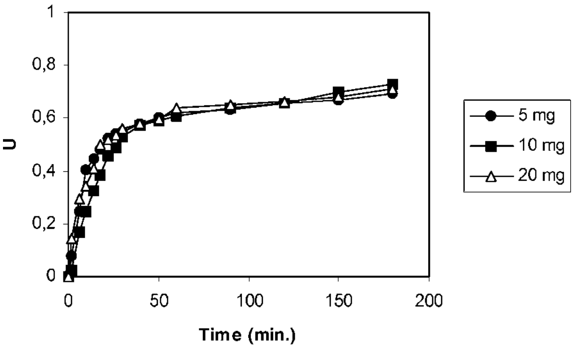

Figure 2. Resin amount effect on retained chromium (pH 5).

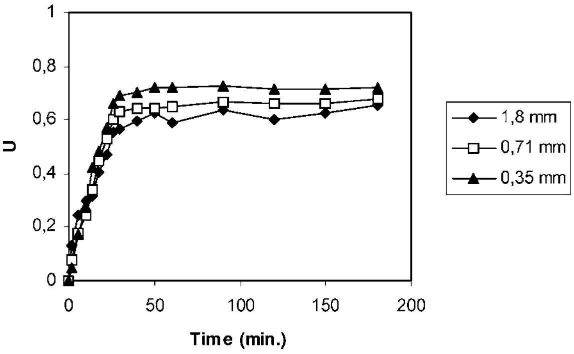

Figure 3. Resin particle size effect on retained chromium (pH 5).

2.6. Interruption Tests

The experiments were run exactly in the same way in the batch experiments, with the only exception that,

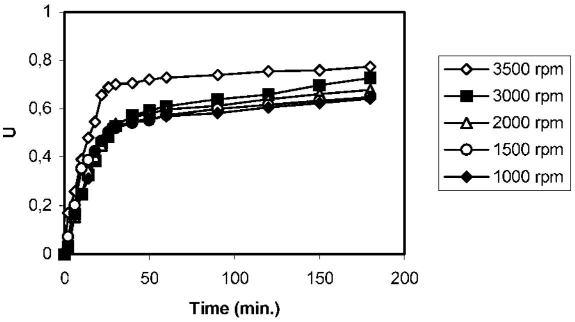

Figure 4. Stirring speed effect on retained chromium (pH 5).

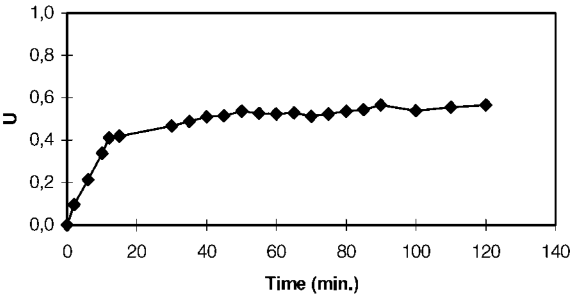

Figure 5. Retained chromium depending on time (pH 5).

after 15 min the reactor (with the resin) is in the reaction batch, the stirrer was extracted from the batch and kept it rotating in the air for 3 min and stopped its rotation. After 15 min interruption, it started again the experiment by re-immersing the reactor in the same solution, and continued to take sample and measured the liquid phase concentration. Measured liquid phase residual concentration, before and after interruption, and plot for each experiment the U vs. t (time) curve. The result is given Fig. 5.

$$(U = C_o - C_t/C_o) \tag{5}$$

(U: Fractional approach to equilibrium, C_o: The beginning concentration of chromium mg L^{-1}, C_t: Concentration of chromium at t time mg L^{-1})

2.7. *Equilibrium Experiments*

Equilibrium experiments were performed with batch procedure. Experiments with respect to sorption equilibria were carried out at constant concentrations in the liquid phase and constant quantities of resins in each of the samples. For the determination of the sorption equilibrium, samples of centrifuged resin material (0.5–3 g) were equilibrated with 200 mL basic chromium sulphate bearing solution having an initial concentration of 0.2 mmol L^{-1} Cr^{3+}. Resin loadings were determined from the difference between initial and equilibrium concentrations. The equilibration was carried out at room temperature (25°C) for one week by shaking time to time. At equilibrium, samples were analyzed for the chromium concentration by means of atomic absorption spectrophotometry. Mean value of the separation factor, $\alpha_{Na/Cr}$ calculated as

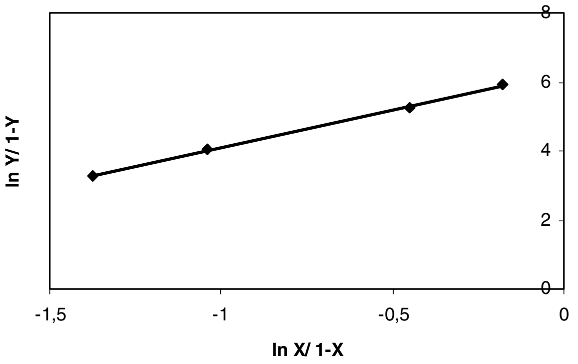

Figure 6. Equilibrium isotherm of Na^+/Cr^{3+} exchange of chelating resin, determination of separation factor.

$$\alpha_{Na/Cr} = Y/(1 - Y)/X/(1 - X) \tag{6}$$

was obtained by the least square method applied to ln-ln plots of Eq. (6), as shown in Fig. 6.

(X: equivalent fraction of Cr^{3+}in solution at equilibrium, Y: equivalent fraction of Cr^{3+} in resin at equilibrium)

3. Results

Experimental results were evaluated according to Nernst-Plank film diffusion control model (fdc) and solid phase diffusion control model (pdc).

3.1. *Effect of Concentration on Kinetics*

Results obtained for Amberlite IRC 718, in the range of 5–160 mg L^{-1} (pH 5) chromium concentrations and they are given in Fig. 1. As shown there, exchange rate increases with solution concentration increases. Although there is a sensible decrease in exchange rate with decreasing stirring speed and liquid phase concentration, confirms the possible rate control by ionic interdiffusion in the Nernstian liquid film around the particle, there is not sharp linearities of the U vs. t

Table 4. The half exchange times, $t_{0.5}$, for the kinetic experiments run on Amberlite IRC 718 at different liquid phase concentration, resin amount, stirring speed and resin bead size.

C (Concentration) (mg L^{-1})	m (resin amount) (mg)	Stirring speed (rpm)	Resin bead size (mm)	$t_{0.5}$ (half exchange times) (min)
5	10	3000	0.35	1
10	10	3000	0.35	8
50	10	3000	0.35	15
75	10	3000	0.35	21
100	10	3000	0.35	27
160	10	3000	0.35	45
160	5	3000	0.35	8
160	10	3000	0.35	16
160	20	3000	0.35	11
160	10	1000	0.35	8
160	10	1500	0.35	10
160	10	2000	0.35	13
160	10	3000	0.35	16
160	10	3500	0.35	18
160	10	3000	0.35	13
160	10	3000	0.71	14
160	10	3000	1.8	15

curves. Smoother concentration gradients in the liquid film, with reducing external concentration, leads to lower driving forces for interdiffusing ions in and out of the film and thus to poorer overall kinetic performances (Helfferich et al., 1985b). The liquid phase mass transfer control was proportional to concentration (C). As evidenced from Table 1, film diffusion control (fdc) model demands the rate to be inversely proportional to the particle radius and ion exchange capacity, and to be proportional to the solution concentration. In addition, at Table 4 is noticed that an important increase in the half exchange times (t_{05}) obtained passing from 1 to 160 mg L^{-1} solution concentration.

3.2. *Effect of Resin Amounts on Kinetics*

Figure 2 shows the effect of resin amounts on kinetics. The resin amounts were taken between 5 to 20 mg. There was not much effect of resin amount on ion exchange kinetics.

3.3. *Effect of Resin Particle Size on Kinetics*

The surface of contact between any sorbent and the liquid phase plays an important role in the phenomena of sorption. If controlled by mass transfer in the liquid, the exchange rate is proportional to the specific surface area and thus is inversely proportional to the particle radius or diameter. The studied resin particle size range was between 0.35 to 1.8 mm and the results are given in Fig. 3. In Fig. 3, fractional uptakes for three particle sizes were plotted against the time. The larger surface area exposed, associated with the smaller size of the particles (particle size was between 0.35 to 1.8 mm), the reduced solid phase diffusional patterns. Accordingly, the exposed surface area of the resin plays a major role in determining the overall kinetics of this resin. Thus, the imperfections in the agreement between experiments and Model 1 strengthen rather than weaken the conclusion that liquid phase mass transfer predominantly controls the rate, with solid phase diffusion causing some retardation at the higher concentration and the larger particle size. We also noticed that the variation in particle size appears to have an influence on the time required to reach equilibrium. Consequently, increasing particle size increases the time needed to reach equilibrium. These observations suggest that the chromium sorption kinetic by resin is largely determined by the particle size.

3.4. Effect of Stirring Speed on Kinetics

In the goal to determine the optimal speed of stirring, the kinetics of chromium removal by Amberlite IRC 718 was studied using stirring speeds ranging from 1000 to 3500 rpm. Figure 4 shows the plots of U versus time at different speeds of the stirrer. The observation that the uptake rate remains dependent of the speed. The sensible increase of the exchange rates with stirring speed (rpm) and liquid phase concentration (C) are additional evidence of the film diffusion control. On the other hand, slower kinetics at low stirring speed can be associated with the formation of a thicker liquid film around the particle, thus to longer diffusional patterns for the ionic interdiffusion in the stationary liquid film determining the overall ion exchange kinetic control. On the basis of Eq. (3), almost equivalent figure for the film thickness was evaluated with both models, which resulted in the range of 1.8×10^{-3} cm.

3.5. Interruption Tests

The interruption experiments were run in the same way of batch experiments, with one exception as explained before. The result is given Fig. 5. After 15 min interruption, when started again the experiments, we could not observe the U vs. t curves having a higher slope in correspondence of 15 min (when the interruption was done). If there was a particle diffusion control (pdc), the kinetics should be faster after reimmersion in the batch. Because of this reason, we can say that there is a possible film diffusion control (fdc).

Exchange capacities and moisture contents of the resin were also determined for two different ionic forms and the results are given Table 3.

3.6. Equilibrium Experiments

Equilibrium experiments were performed as explained at 2.7. Figure 6 shows equilibrium isotherm for Cr uptake by Na form resin investigated and separation factor ($\alpha_{\mathrm{Na/Cr}}$) was calculated as 1.99 from Eq. (6). As can be seen Fig. 6 that the mean value of $\alpha_{\mathrm{Na/Cr}}$, quite constant obtained for the resin by linear regression analysis of experimental points, is highly representative of the whole isotherm. There was extremely high chromium selectivity occur, with a regular increase of $\alpha_{\mathrm{Na/Cr}}$ value. The separation factor, corresponding to the uptake of a highly preferred counterion. For $\alpha_{\mathrm{BA}} \geq 1$ and not too small values of $1 - U$, the left side of Eq. (2) is dominated by the second term and the equation reduces to Eq. (3). This reflects a linear dependence of fractional conversion on time, i.e., a constant rate of exchange. The physical explanation is simple. With very high preference for the counterion being taken up, that ion's concentration in solution, at the solution exchanger interface remains negligible until conversion is almost complete. According to Eqs. (2) and (3), the time required for any given conversation is also proportional to particle radius and ion exchange capacity. The size dependence reflects the fact that the surface are per unit volume of particles is inversely proportional to the particle radius or diameter.

After kinetic experiments and interruption tests, some correlations were done with t_{05} (half exchange times) vs. concentration (C), stirring speed (rpm), bead radius and diameter (r^0, r^{02}) for Amberlite IRC 718. The results are given in Table 4. Generally speaking for all resins the correlations of t_{05} (half exchange times) vs. concentration (C), which should give linear trends in case of film diffusion control (fdc) (4). The linear plots of the half exchange times vs. liquid-phase concentration and stirring speed and the negative interruption test on this system are other points in favour of the film interdiffusion as the rate determining step for the overall kinetic process. Also there are evidences of particle diffusion control (pdc) on the basis of t_{05} (half exchange times) correlations vs. bead radius and diameter (r^0, r^{02}). In all experiments and comments possible conclusion could be that possibly both mechanism (fdc + pdc) control kinetics on Amberlite IRC 718.

Figures 7 and 8 show the linear correlation of half exchange times vs. concentration. The sensible increase of exchange rates with liquid phase concentration, C and stirring speed (rpm), and the linear correlations

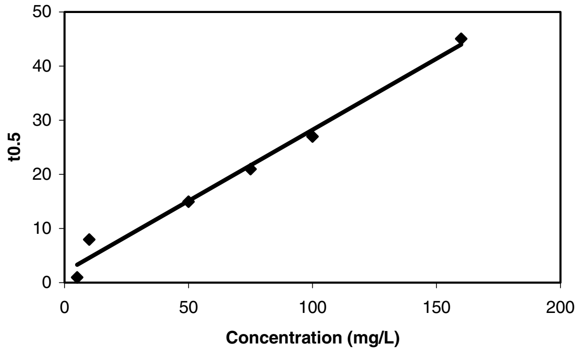

Figure 7. Linear correlation of half exchange times vs. concentration.

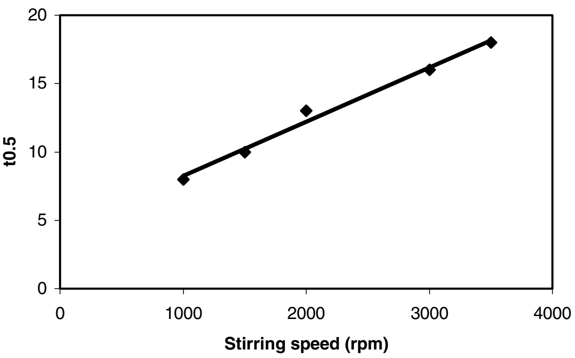

Figure 8. Linear correlation of half exchange times vs. stirring speed.

of the mentioned parameters vs. the half-times of exchange, $t_{0.5}$ are additional evidence in favor of the film diffusion control.

4. Conclusion

After kinetic experiments and interruption tests, some correlations were done with t_{05} (half exchange times) vs. concentration (C), stirring speed (rpm), bead radius and diameter (r^0, r^{02}) for Amberlite IRC 718. Results are shown that although t_{05} vs. stirring speed (rpm) and liquid concentration (C) trend appear almost straight, bead radius and diameter (r^0, r^{02}), both appear slightly linear. Both these findings should lead to possible particle diffusion control (pdc). In the other side, there is no faster kinetics after re-immersion into the reaction batch in the interruption test. It shows that a possible film diffusion control (fdc). As a conclusion could be that possibly both mechanisms (fdc + pdc) control kinetics on this resin. The exchange rate is essentially controlled by film diffusion control (fdc), but is affected under some conditions to various degrees by solid phase diffusion. This conclusion has resulted from determination of exchange rates at different solution concentration, particle size, resin amount and stirring speed.

Nomenclature

fdc	Nernst plank film diffusion control model
pdc	Solid phase diffusion control model
U	Fractional attainment of equilibrium
t	Time (min)
J	Flux of counterion (mmol cm^{-2} s^{-1})
D	Effective liquid-phase diffusivity (cm^2 s^{-1})
ΔC	Concentration difference of counterion across film (mmol cm^{-3})
δ	Film thickness (cm)
R	Gas constant (coulomb V mmol^{-1} deg^{-1})
T	Temperature (K)
z_i	Electrochemical valance of counterion i
φ	Electric potential (V)
C_o	The beginning concentration of chromium (mg L^{-1})
C_t	Concentration of chromium at t time (mg L^{-1})
t_{05}	Half exchange times
r^0	Bead radius (mm)
r^{02}	Bead diameter (mm^2)
C	Ion exchange capacity of of resin (eq L^{-1})
α_{BA}	Separation factor for counterion A in the solution phase and counterion B in the resin phase
X	Equivalent fraction of Cr^{3+} in solution at equilibrium
Y	Equivalent fraction of Cr^{3+}in resin at equilibrium

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