

## A kinetic investigation of removal of chromium from aqueous solutions with a strong cation exchange resin

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**Abstract** A kinetic investigation was performed with an ion exchange resin for chromium. A strong cation exchange resin (Amberlite IR 120) was used for removal of chromium. The effects of concentration, resin amount, and stirring speed on kinetics were investigated. The metal concentration range studied was between 5 to 160 mg/dm<sup>3</sup> (the amount of solution was 4 dm<sup>3</sup>), the resin amount range was between 5 to 20 mg, and the stirring speed range was between 1000 to 3500 rpm. Equilibrium experiments were performed for calculation of separation factor. 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), respectively were identified, and the dependence of the rate on parameters such as solution concentration, resin amount, stirring speed, etc. was examined for each of them. The interpretation of these data shows that the system is probably controlled by both film and particle diffusion.

**Keywords** Kinetics; Strongly acidic cation exchange resin; Chromium; *Kressman-Kitchener* stirrer reactor.

### Introduction

Ion exchange is a heterogeneous chemical reaction. Ions in the liquid phase are exchanged with

ions in the solid phase. In an ordinary ion exchange process, the counter-ions of different species exchange with each other. In this case the co-ions in the system do not undergo any changes. As a result, the total concentration of counter-ions and co-ions remains constant before and after exchange [1]. As in other heterogeneous reactions between solid and liquid phase, there are a number of sequential processes that determine the rate of reaction:

1. Diffusion of ions through the liquid film surrounding the particle.
2. Diffusion of ions through the polymeric matrix of the resin.
3. Chemical reaction with the functional groups attached to the matrix.

One of the steps usually offers much greater resistance than the others, so it can be considered as the limiting step of the process [2]. There are only a few cases in which the rate of ion exchange is determined by a chemical reaction. When the exchange process is in its initial stage, it is generally assumed that the chemical reaction is infinitely fast. *Helfferrich* gave eleven examples in which chemical reactions have an influence on the rate of exchange; they are all related with some kind of parallel ionic reaction that changes the identity of the ions involved [3].

In many cases, ion exchange kinetics is limited by the step of diffusion inside the particle. When convection in the solution is low and/or the degree of polymer cross-linking is low, it is likely that the main resistance to diffusion can be found in the

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liquid phase. As the degree of cross-linking grows, resins are more compact, so the mass transfer inside the particles is more difficult and particle diffusion may become the rate controlling step.

## Results and discussion

### Theoretical considerations

#### Film diffusion rate control (fdc)

It is assumed that ions find the main resistance to diffusion in a thin film of solution that surrounds the particle surface. The driving force of the mass transfer is assumed to be linear and ions are homogeneously distributed inside the particle [4–6]. The mass transfer coefficient depends on the diffusivity of ions in the solution and the thickness of the film.

For dilute solutions in which film diffusion tends to be the rate-controlling step, the film thickness depends on both the flow rate and the degree of agitation.

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

$$J = D\Delta C/\delta \quad (1)$$

Equation (1) integrated, yields

$$\ln(1 - U) + (1 - \alpha_{BA})U = -3DC\alpha_{BA}t/r^0\delta\bar{C} \quad (2)$$

of special interest in the present context is the limiting case with very large value of the separation factor  $\alpha_{BA}$ , corresponding to the uptake of a highly preferred counterion. For  $\alpha_{BA} \geq 1$  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:

$$U \approx 3DCt/r^0\delta\bar{C} \quad (3)$$

This reflects a linear dependence of fractional conversion on time, *i.e.*, a constant rate of exchange [7].

This model predicts concentrations depending on: total ionic concentration in solution, particle size,

stirring of the solution, equilibrium isotherms, nature of ion exchange resin, and nature of co-ions present in the solution.

#### Particle diffusion rate control (pdc)

Ions are homogeneously distributed inside the particle. The external surface of the bead is in direct contact with the surrounding solution, and they are in chemical equilibrium. The driving force of the mass transfer is the concentration difference between the external surface of the particle and the average concentration inside the bead.

The mass transfer coefficient  $K_s$ , depends on the effective diffusivities of the ions inside the particle, and on the thickness of the area of mass gradient. The kinetic curves are dependent on particle size and nature of ion exchange resin [2].

The model describes diffusion with the *Nernst-Planck* equations [7];

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

which account for electric potential gradient,  $\text{grad } \varphi$ , 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.

Models 1 and 2 additionally assume that no reactions involving the exchanging ions or fixed groups occur. Table 1 shows, the effects of experimental variables on the ion-exchange rate controlled by intraparticle diffusion and by liquid-phase mass transfer.

Chromium is introduced into the natural bodies of water from industries like electroplating, leather tanning, cement industries, steel industries, and photog-

**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 $1/r^{0.2}$
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

raphy [8]. Ion exchange is now widely used for treating waste rinse water from the different industries.

Ion exchange may also be considered a statistical redistribution of ions between the exchanger and the contacting liquid phase, with rates usually controlled by the resistance to mass transfer in the solid or the liquid phase or both [9]. Accordingly, ion exchange kinetics has been described in terms of *Fick's* laws, with rates depending on the ion concentration gradients in the respective media [10, 11]. Because of their electrical charges, ions are also subject to the electric field generated by their diffusion. The resulting electric transference is superimposed on the ordinary diffusion driven by the concentration gradient, as described by the *Nernst-Planck* theory [9]. The original *Nernst-Planck* theory did not include effects such as variation of individual ionic diffusivities, specific interactions (chemical reactions), transport of co-ion and solvent, or reactions which the exchanging ions or the fixed groups might undergo. Moreover, it was at first applied only to binary systems. In 1965, a mathematical description of binary ion exchange processes accompanied by fast chemical reactions was first offered [3, 12] and experimental verification of predictions made on this basis was undertaken by some researchers [13–24].

A large number of practical applications of ion exchange to environmental protection involve multi-component systems and, most importantly, specific interactions in the solid phase between the mobile species and the fixed groups. This research area has received particular interest in the last decade as the need to close the gap between existing theory and practical needs became more pressing [9].

In this study, ion exchange kinetics in batch system was studied using the strong cation exchange resin Amberlite IR 120. The previous batch experiments have given some information for helping to these kinetic experiments [25, 26]. The effect of concentration, resin amount and stirring speed on kinetics were investigated and the results compared with existing kinetic models, that is *Nernst-Planck* film diffusion control model (fdc) and solid phase diffusion control model (pdc).

#### *Kressman-Kitchener* stirrer system

Kinetic determinations were made by means of a modification of the *Kressman-Kitchener* stirrer reactor technique [27, 28]. 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 withdrawn at various intervals) to proper equations [29].

#### Interruption tests

The interruption test is another method for determining the rate controlling mechanism [27]. 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 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.

#### Results on Amberlite IR 120

Results obtained for Amberlite IR 120, in the range of 5–160 mg/dm<sup>3</sup> (pH 5) chromium(III) concentrations 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, which confirms the possible rate control by ionic interdiffusion in the Nernstian liquid film around the particle, there are not sharp linearities of the  $U$  vs.  $t$  curves. Smoother concentration gradients in the liquid film, with reducing external concentration, leads to lower driving forces for inter-diffusing ions in and out of the film and thus to

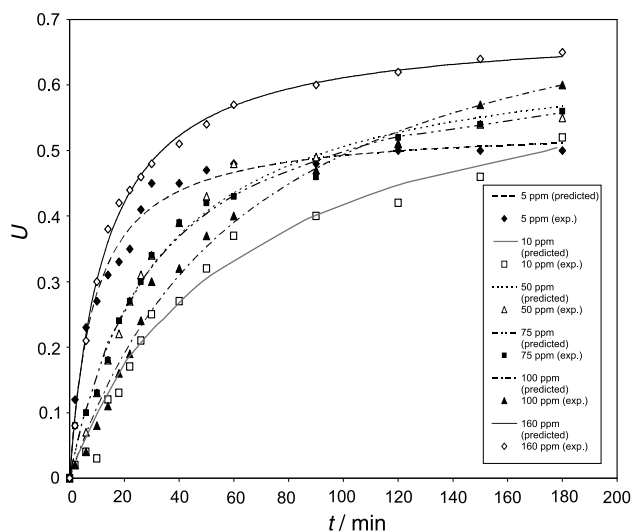


Fig. 1 Concentration effect on retained chromium (pH 5)

poorer overall kinetic performances [28]. The slope of  $U$  with time indicates a possible film diffusion control. The liquid phase mass transfer control was proportional to concentration ( $C$ ). As evident 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, in Table 2 is noticed that an important increase in the half exchange times ( $t_{0.5}$ ) is obtained passing from 1 mg/dm<sup>3</sup> to 160 mg/dm<sup>3</sup> solution concentration.

Table 2 The half exchange times,  $t_{0.5}$ , for the kinetic experiments run on Amberlite IR 120 at different liquid phase concentration, resin amount, stirring speed

C (concentration) mg/dm <sup>3</sup>	m (resin amount) mg	Stirring speed rpm	Resin bead size m	$t_{0.5}$ (half exchange times) min
5	10	3000	0.3	9
10	10	3000	0.3	13
50	10	3000	0.3	22
75	10	3000	0.3	22
100	10	3000	0.3	30
160	10	3000	0.3	35
160	5	3000	0.3	11
160	10	3000	0.3	13
160	20	3000	0.3	11
160	10	1000	0.3	9
160	10	1500	0.3	11
160	10	2000	0.3	13
160	10	3000	0.3	15
160	10	3500	0.3	17

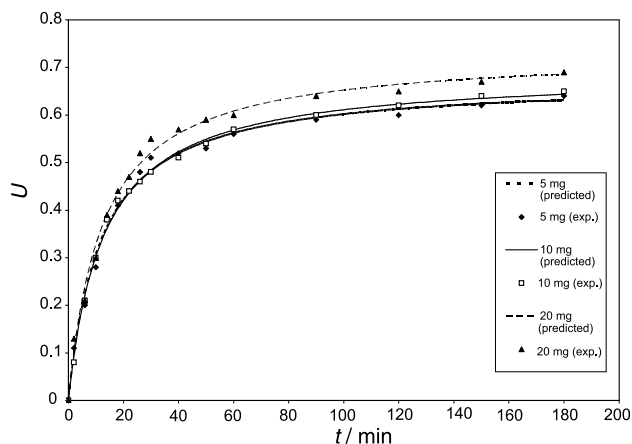


Fig. 2 Resin amount effect on retained chromium (pH 5)

Figure 2 shows the effect of resin amounts on kinetics. The resin amounts were taken between 5 and 20 mg. There was not much effect of resin amount on ion exchange kinetics. Strictly speaking, the amount of resin should not affect the intrinsic kinetics, but should indeed affect the position of the final equilibrium.

Stirring speed range was varied between 1000 and 3500 rpm. Figure 3 shows the plots of  $U$  versus time at different speeds of the stirrer. The observation was 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 ex-

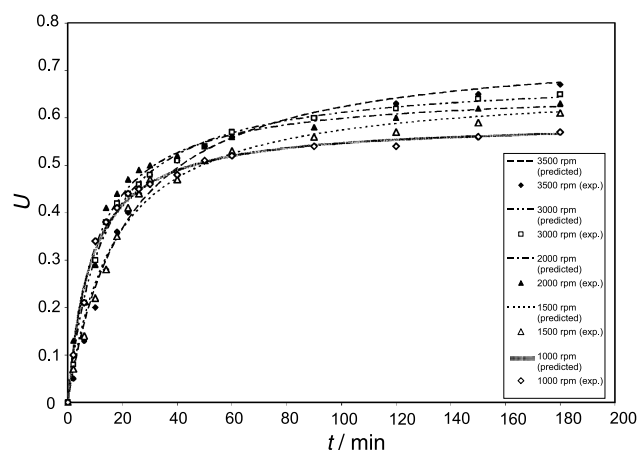


Fig. 3 Stirring speed effect on retained chromium (pH 5)

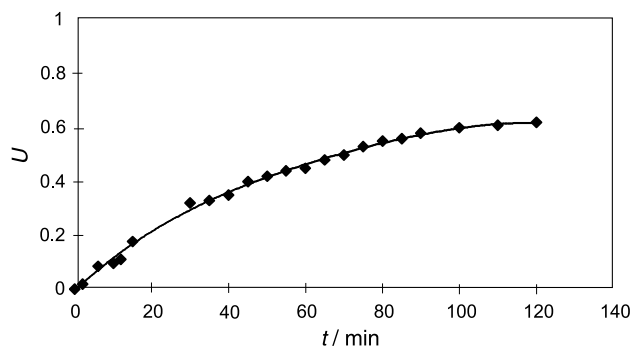


Fig. 4 Retained chromium depending on time (pH 5)

change kinetic control. On the basis of Eq. (3), an almost equivalent figure for the film thickness was evaluated with both models, which resulted in the range of  $1.6 \times 10^{-3}$  cm.

The interruption experiments were run in the same way of batch experiments, with one exception as explained before. The result is given in Fig. 4. After 15 min interruption, the experiments started again, and we observed the  $U$  vs.  $t$  curves having an higher slope in correspondence of 15 min (when the interruption was done). The polarization of the ionic species at the external boundary of the resin bead relaxes and thus the kinetics should be faster after re-immersion in the batch. So, we can say that there was a possible particle diffusion control (pdc).

Table 3 Chromium exchange capacities and moisture contents of the resin

Resin (Amberlite IR 120)	Na <sup>+</sup> form	H <sup>+</sup> form
Capacity (eq./dm <sup>3</sup> ) (column)	1.12	0.97
Moisture content (%)	47.45	55.20

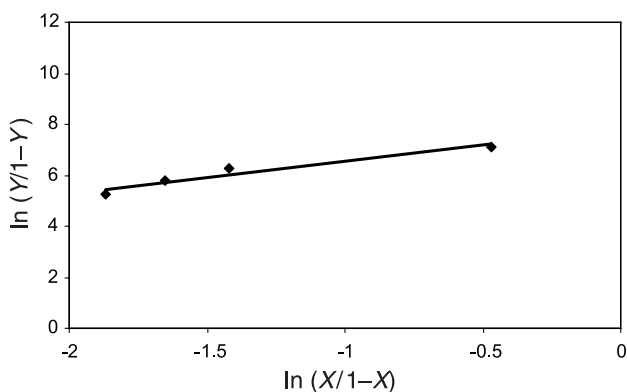


Fig. 5 Equilibrium isotherm of Na<sup>+</sup>/Cr<sup>3+</sup> exchange of Amberlite IR 120 resin, determination of separation factor

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

Equilibrium experiments were performed as explained at Materials and methods. Figure 5 shows equilibrium isotherm for Cr uptake by Na form resin investigated. The separation factor ( $\alpha_{Na/Cr}$ ) calculated as Eq. (6) was obtained by the least square method applied to  $\ln$ - $\ln$  plots of Eq. (6) as

$$\ln[Y/(1-Y)] = \ln \alpha_{Na/Cr} + \ln[X/(1-X)] \quad (7)$$

and separation factor ( $\alpha_{Na/Cr}$ ) was calculated as 1.2512 from the graphic. As can be seen in Fig. 5, the mean value of  $\alpha_{Na/Cr}$ , quite constant obtained for the resin by linear regression analysis of experimental points, is highly representative of the whole isotherm. There occurred extremely high chromium selectivity, with a regular increase of the  $\alpha_{Na/Cr}$  value, the separation factor, corresponding to the uptake of a highly preferred counterion. For  $\alpha_{BA} \geq 1$  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. 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 conversion is also proportional to particle radius and ion exchange capacity. The size dependence reflects the fact that the surface 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  $t_{0.5}$  (half exchange times) vs. concentration ( $C$ ) and stirring speed (rpm) for Amberlite IR 120. The results are given in Table 2. Generally speaking for all resins the correlations of  $t_{0.5}$  (half exchange times) vs. concentration ( $C$ ) should give linear trends in case of film diffusion control (fdc) [7]. The linearity shows a possible film diffusion control in our case. Also there are evidences of particle diffusion control (pdc) on the basis of  $t_{0.5}$  (half exchange times) correlations vs stirring speed (rpm). In all experiments and comments possible conclusion could be that possibly both mechanism (fdc + pdc) control kinetics on Amberlite IR 120.

## Conclusion

After kinetic experiments and interruption tests, some correlations were done with  $t_{0.5}$  (half exchange times) vs. concentration ( $C$ ) and stirring speed (rpm) for Amberlite IR 120. The results of kinetic experiments showed that there was a possible film diffusion control (fdc). On the other side, there was faster kinetics after re-immersion into the reaction batch in the interruption test. As a result of interruption test, there was a possible particle diffusion control (pdc). 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. The stirring speed in the exchange vessel was effected the rate of exchange due to its effect on film thickness. A higher rate of stirring tends to reduce the film thickness.

## Materials and methods

### *Ion exchange resin, reagents, solutions, and equipment*

A strong cation exchange resin, Amberlite IR 120 (Rohm and Haas Co.) was used for the experiments. Table 4 shows the physicochemical properties of the resin. This resin was prepared in  $\text{Na}^+$  form. The stock solutions were prepared from reagent grade basic chromic sulfate  $[\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2]$  that was supplied by Merck (Darmstadt, Germany) and was used at different solution concentration levels. All other chemicals (HCl, NaOH, and NaCl) were obtained from Merck (Darmstadt, Germany). Freshly prepared solutions were used throughout the experiments. High-quality water (18 M $\Omega$ ) obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA) was used to prepare all the solutions and to rinse the previously cleaned laboratory materials. Kinetic determinations were run 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. An air-acetylene flame was used for determination of chromium

amounts in the aqueous phase with the following settings: wavelength: 357.9, lamp current: 7 mA, slit: 0.2 nm, air/acetylene ratio: 3.5/1.5.  $pH$  values were measured during the experiments with a  $pH$ -meter (Metrohm) and a combined glass electrode.

### *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. The conditioned resin was dried under vacuum (40°C, 10 mm Hg) and stored in dry atmosphere.

### *Determination of the resin moisture content*

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

### *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/dm<sup>3</sup> chromium(III) solution. The results are given in Table 3 together with the determined moisture content.

### *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/dm<sup>3</sup>, the resin amount range was between 5 to 20 mg, and 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

**Table 4** The main physicochemical properties of the resin investigated

Resin	Functional group	Bead size mm	Matrix	Moisture holding capacity		Total exchange capacity	
				%		eq./dm <sup>3</sup>	
Amberlite IR 120	Sulfonic	0.3–0.8	Styrene	$\text{Na}^+$ form 44–49	$\text{H}^+$ form 51–56	$\text{Na}^+$ form ≥2.00	$\text{H}^+$ form ≥1.80

box, a weighed amount of  $\text{Na}^+$  form resin sample (about 10 mg) was loaded in the reactor which was immersed while rotating into the reaction batch containing  $1 \text{ dm}^3$  of basic chromium sulfate solution ( $\text{pH}$  5), at pre-determined concentration (*i.e.*,  $5\text{--}160 \text{ mg/dm}^3$ ). 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 the system and the results were compared with existing kinetic models. The results are given in Figs. 1–3.

#### Interruption tests

The experiments were run exactly in the same way as in the batch experiments, with the only exception that, after 15 min the reactor (with the resin) is in the reaction batch, the stirrer was extracted from the batch and kept rotating in the air for 3 min, and its rotation was stopped. After 15 min interruption, it started again the experiment by re-immersing the reactor in the same solution, and continued to take samples and measure the liquid phase concentration. Liquid phase residual concentration was measured before and after interruption, and for each experiment the  $U$  vs.  $t$  (time) curve was plotted. The result is given in Fig. 4.

$$(U = C_0 - C_t/C_0) \quad (5)$$

( $U$ : Fractional approach to equilibrium,  $C_0$ : The beginning concentration of chromium,  $\text{mg/dm}^3$ ,  $C_t$ : Concentration of chromium at  $t$  time,  $\text{mg/dm}^3$ )

#### 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  $200 \text{ cm}^3$  basic chromium sulfate bearing solution having an initial concentration of  $0.2 \text{ mmol/dm}^3 \text{ Cr}^{3+}$ . Resin loadings were determined from the difference between initial and equilibrium concentrations. The equilibration was carried out at room temperature ( $25^\circ\text{C}$ ) 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,  $\alpha_{\text{Na/Cr}}$  calculated as

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

was obtained by the least square method applied to  $\ln\text{--}\ln$  plots of Eq. (6), as shown in Fig. 5.

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

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