



The Kinetics of Uptake of Cu⁺⁺ Ions in Ionac SR-5 Cation Exchange Resin

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Abstract. The kinetics of sorption of Cu⁺⁺ ions in a typical cation exchange resin (IONAC SR-5) have been studied by two methods; the traditional batch method which involves following the change in Cu⁺⁺ concentration in a solution of finite volume in contact with the resin, and by removing and sectioning individual resin particles to follow the progress of the adsorption front. The results obtained by both methods are consistent. The equilibrium isotherm for this system is of highly favorable (Langmuir) form and the uptake kinetics show a clear transition from linear Fickian behavior at low concentrations to irreversible (shrinking core) behavior at high concentrations. The addition of ammonia to the system has little effect on the equilibrium isotherm but the intraparticle diffusivity is increased by a factor of about four. This may be due to reduction in the degree of hydration of the cuprammonium ion in comparison with uncomplexed Cu⁺⁺.

Keywords: diffusion, ion exchange, ionac resin, sorption kinetics, Cu⁺⁺ ions

Introduction

Cation exchange resins are widely used for removal of trace concentrations of metal ions in the purification of boiler feed water and sometimes of potable water (Radecki et al., 1999). The equilibrium isotherms have been widely reported and the kinetics have also been studied, but less extensively—see for example Gabai et al. (1998) and Rao et al. (1982). The actual ion exchange process is rapid and hydrogen (or H₃O⁺) ions diffuse rapidly, so the overall process is generally controlled by diffusion of the exchanging cation through the pores of the polymeric resin. The process is therefore formally similar to physical adsorption and can be modeled as a diffusion process and characterized by an “effective” diffusivity. Gabai et al. correlated their kinetic data using the normal Fickian diffusion model whereas Rao et al. used the “shrinking core” diffusion model. The present study was undertaken as part of an experimental study of a novel type of continuous mass transfer device. The resin selected (IONAC SR-5 supplied by Sybron Corporation) has a very high affinity for heavy metal ions, thus allowing measurements to be made over a wide range of concentrations. For

convenience, Cu⁺⁺ was selected for study, since the intense blue color of the solution in presence of aqueous ammonia affords a simple and accurate means of monitoring even at low concentration levels.

Our initial intention was to make only a preliminary study to provide an order of magnitude estimate of the intra particle diffusion rate. However, the kinetic behavior proved sufficiently interesting to merit more detailed study since, at higher concentrations, this system provides an excellent example of shrinking core behavior, while at low concentrations the linear Fickian model applies.

Equilibrium Isotherm

The equilibrium isotherm, shown in Fig. 1, was determined by the standard batch uptake method. 1 g of resin was added to each of a series of vials containing 10 ml of aqueous copper sulfate solution at various concentrations varying from 2 × 10⁻⁴ g Cu/ml to 0.04 g Cu/ml. The vials were allowed to equilibrate with occasional shaking and the concentration of Cu⁺⁺ in solution was followed using a Hach DR 2000 Direct

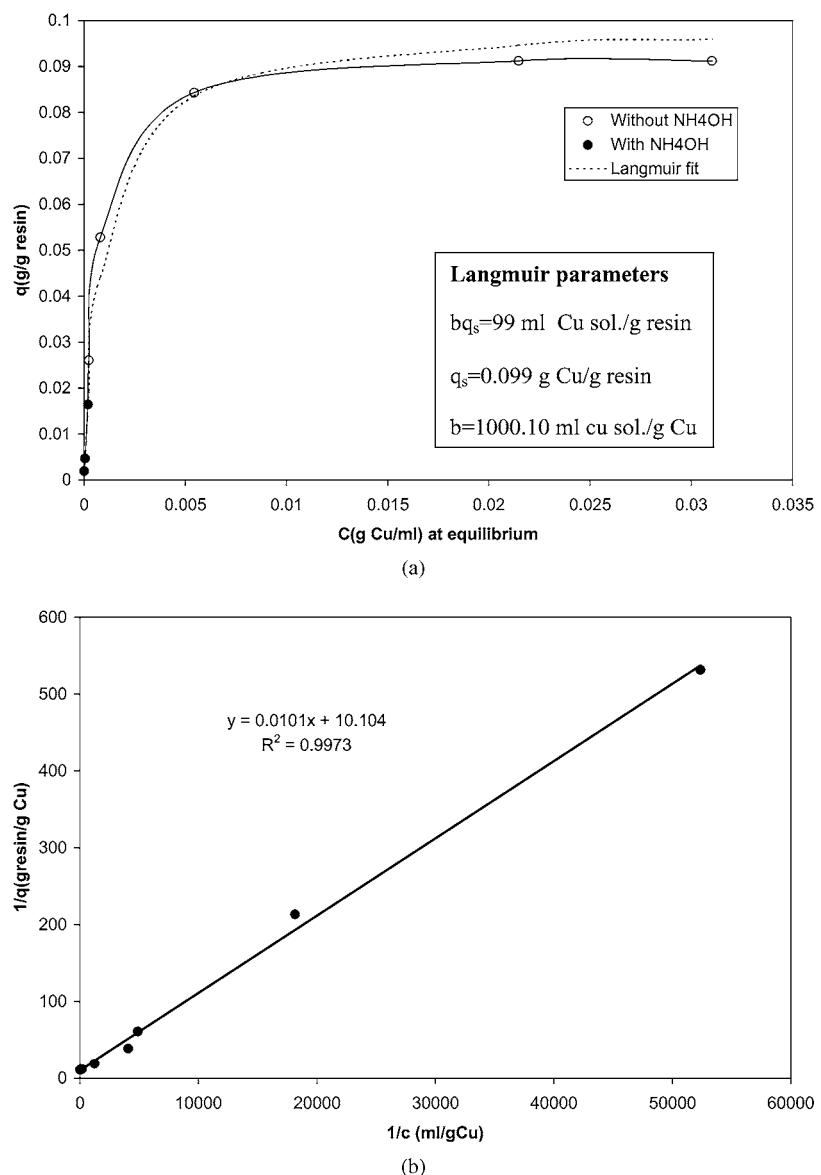


Figure 1. (a) Equilibrium isotherm for Cu^{++} in IONAC SR-5 resin at 25°C showing experimental points and fit of Langmuir isotherm expression (Eq. (1)) with the specified parameters. (b) Langmuir plot of the isotherm data.

Read spectrophotometer set at a wavelength of 620 nm. The linearity of the relationship between the spectrometer reading and the concentrations was checked experimentally. The uptake on the resin at equilibrium was calculated by material balance.

To achieve greater accuracy at the lower concentration a small excess of ammonia was added. Replicate measurements with and without ammonia at a solution concentration of 2×10^{-4} g Cu/ml, showed no measurable difference in the uptake of copper, showing that the

equilibrium is not significantly affected by the presence of NH_3 (see Fig. 1).

The isotherm is of highly favorable form and can be represented fairly well by the ideal Langmuir model:

$$\frac{q}{q_s} = \frac{bc}{1 + bc} \quad (1)$$

The fit of this expression to the experimental data with the given values of the parameters b and q_s

is indicated by the dotted line in Fig. 1(a) and the Langmuir plot ($1/q$ vs $1/c$) is shown in Fig. 1(b).

Theoretical Uptake Curve

The uptake rate is controlled by diffusion of the hydrated Cu⁺⁺ ions through the polymer matrix. For a linear system the expression for the uptake curve for adsorption from a well-mixed solution of finite volume has been given by Crank (1956).

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6(1-\alpha)e^{(-D_c q_n^2 t / R_p^2)}}{9\alpha + q_n^2(1-\alpha)^2} \quad (2)$$

where α represents the fraction of sorbate initially present in the solution which is ultimately adsorbed and q_n is given by the roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \left(\frac{1-\alpha}{\alpha}\right)q_n^2} \quad (3)$$

When the isotherm is so strongly favorable that it can be considered as irreversible or rectangular the diffusional behavior is quite different. The concentration profile assumes the form of a shock front which advances at a velocity controlled by diffusion of the sorbate through the outer, saturated shell. This is commonly called "shrinking core" behavior. A detailed review of the kinetics for such a system has been given by Suzuki (1990).

The uptake curve, for sorption from a system of finite volume, is given by:

$$\frac{DC_0 t}{R_p^2 q_s} = \int_{z=1}^z \frac{z(1-z)}{1-\alpha + \alpha z^3} dz \quad (4)$$

Where $z = r/R_p$ represents the (dimensionless) radius of the shock front (see Fig. 2) and $\alpha = V_s q_s / V_i C_0$ represents the fraction of the sorbate initially present in the solution which is ultimately adsorbed. Since z is related to the fractional uptake by:

$$\frac{m_t}{m_\infty} = 1 - z^3 \quad (5)$$

Equation (3) defines the dimensionless uptake curve (m_t/m_∞ vs $DC_0 t / R_p^2 q_s$ for any specified value of α). A family of uptake curves calculated in this way is given in Fig. 3. The formal derivation of Eq. (4) is summarized in the Appendix.

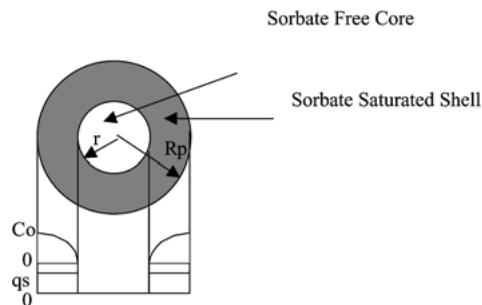


Figure 2. Schematic diagram showing the shrinking core diffusional behavior characteristic of adsorption with a rectangular isotherm.

Measurement of Uptake Curves

Uptake rates were determined by the batch method. A measured quantity of dry resin (3.7 to 5 g) was added at the start of the run to a 250 ml Erlenmeyer flask. Brief details of the resin are summarized in Table 1. The solution was agitated using a magnetic stirrer. Small resin free samples were withdrawn periodically using a pipette and analyzed spectrophotometrically. The experiment was repeated, under similar conditions, with two different resin size fractions (runs 1 and 2) and in the presence of ammonia (runs 3 and 4). Runs 5 and 6 were carried out at higher concentration levels and run 7, which was carried out at a concentration of 0.006 g Cu/ml, utilized an entirely different approach. At this level of concentration the equilibrium isotherm is effectively rectangular so one can expect shrinking core behavior. A dozen large (1.2 mm particles) were selected and each particle was immersed in the copper solution for a different time. At the end of that time the particle was removed, cut in half with a razor blade and examined on an imaging microscope. The blue copper saturated layer showed very clearly (see Fig. 4) and the progress of the advancing front could

Table 1. Resin properties. [Sybron].

Resin	IONAC-SR5
Polymer structure	Styrene divinylbenzene copolymer
Functional group	Iminodiacetic acid
Physical form	Spherical beads
Selective copper capacity (meq/ml) ^a	1.3 (Na form)
Effective size (mm)	0.47–0.53

^aBased on copper uptake from an aqueous solution containing 3750 ppm Cu (as CuCl₂) and 10% NaCl.

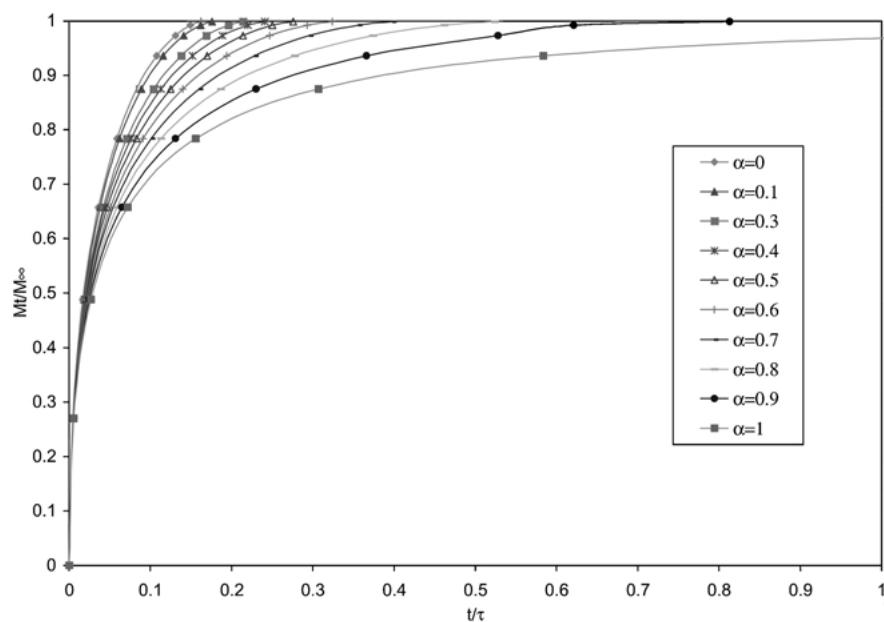


Figure 3. Theoretical uptake curves for irreversible adsorption from a system of finite volume.

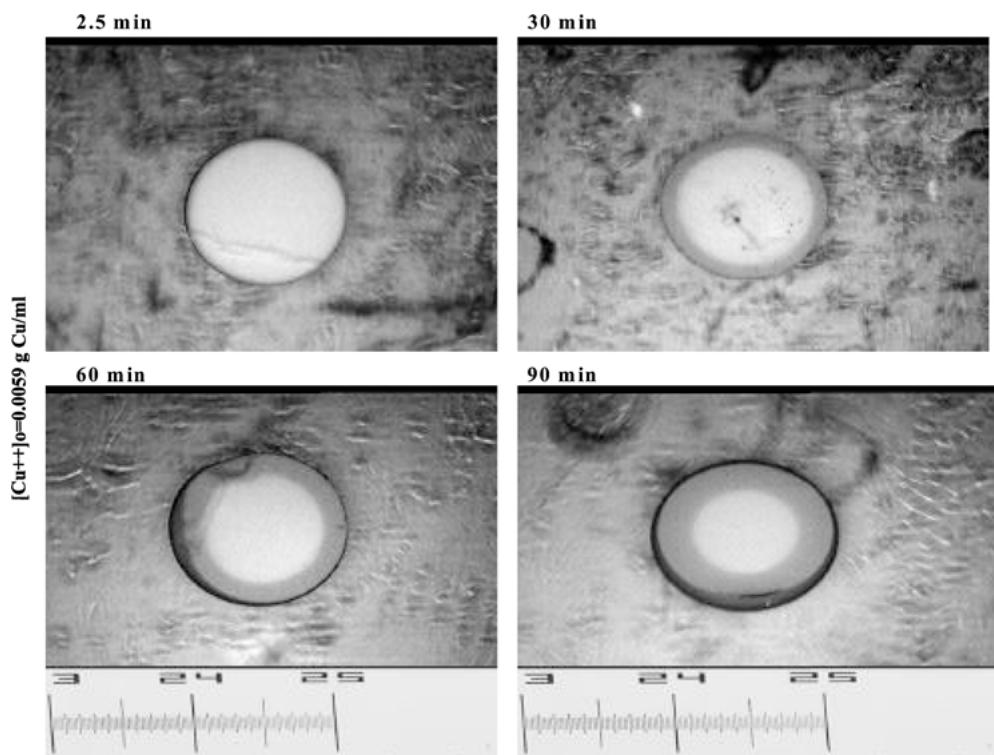


Figure 4. Shrinking core behavior. Sequential photographs showing sections through a resin particle after exposure to the copper solution for different times.

be easily measured, thus providing direct experimental confirmation of the shrinking core behavior.

Results and Discussion

Brief details of the experimental runs together with the derived parameters are summarized in Table 2. Runs 1–4 were performed at low concentrations within the Henry's law region and the resulting uptake curves were therefore analyzed according to Crank linear model for adsorption from a solution of finite volume (Eqs. (2) and (3)).

Figure 5 shows the uptake curves for runs 1 and 2. It is evident that the simple linear diffusion model provides a good representation of the observed behavior and the effect of particle size is correctly predicted. Runs 3 and 4 which were carried out under conditions similar to runs 1 and 2 but in the presence of ammonia show that the uptake rate is greatly enhanced (see Fig. 6). For the smaller particles the rate was too fast for reliable measurements but the effect of particle size is clearly evident and the data appear to be at least approximately consistent with the linear diffusion model but with a diffusivity that is substantially increased relative to runs 1 and 2.

Table 2. Summary of uptake rate measurements and derived parameters.

Run #	R_p (cm)	C_0 (g Cu/ml)	α	$\lambda = q_t/q_s$	q_0/C_0	D_e/R_p^2 (s ⁻¹)	D_e (cm ² /s)	D (cm ² /s)
1	0.018	0.00019	0.5	0.08	100	1.58×10^{-4}	5.1×10^{-8}	5×10^{-6}
2	0.038	0.00019	0.5	0.09	100	3.58×10^{-5}	5.1×10^{-8}	5×10^{-6}
3	0.018	0.00019	0.8	0.04	100	6.2×10^{-4}	2×10^{-7}	2×10^{-5}
4	0.038	0.00019	0.8	0.02	100	1.4×10^{-4}	2×10^{-7}	2×10^{-5}
5	0.018	0.0019	0.35	0.52	40	3.8×10^{-5}	1.2×10^{-8}	4.8×10^{-7}
6	0.038	0.0059	0.55	0.73	24	1.2×10^{-5}	1.7×10^{-8}	4.1×10^{-7}
7	0.06	0.0059	0	0.85	14.5	1.05×10^{-5}	3.8×10^{-8}	5.5×10^{-7}

λ is based on final (equilibrium) value of q . q_0/C_0 represents the average value of this ratio. For the low concentration runs this corresponds to K .

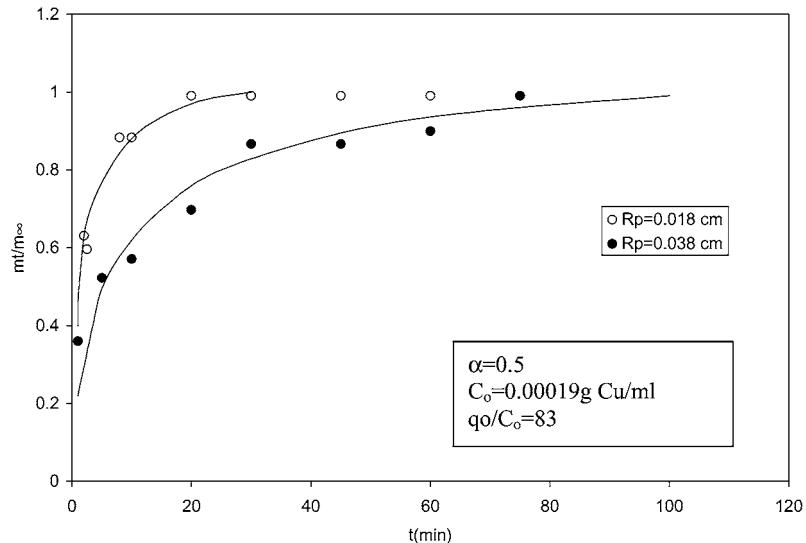


Figure 5. Experimental uptake curves for runs 1 and 2 showing effect of particle size on the uptake kinetics. These experiments are at low concentration within the linear regime. The theoretical curves are calculated from Eq. (2) with the parameters given in Table 2.

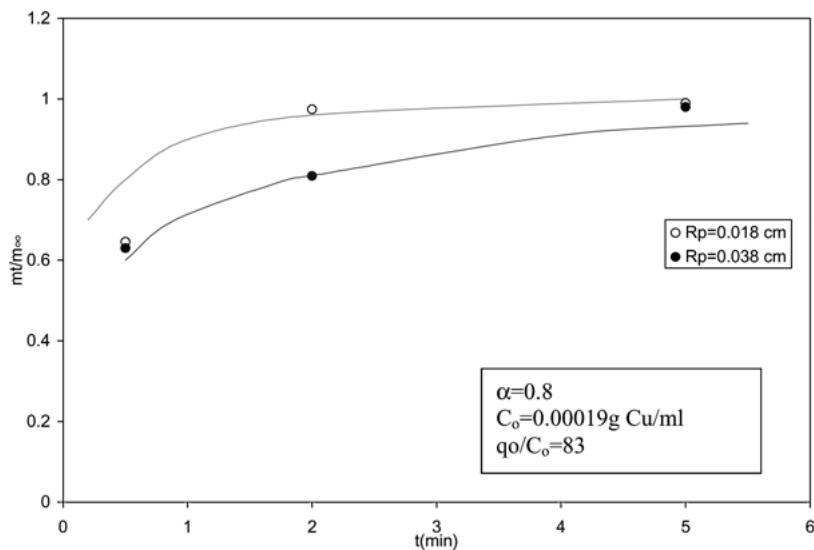


Figure 6. Uptake curves for runs 3 and 4 showing the effect of ammonia on the uptake rate (compare with Fig. 5). Theoretical curves are calculated from Eq. (2) (linear model) with the parameter given in Table 2.

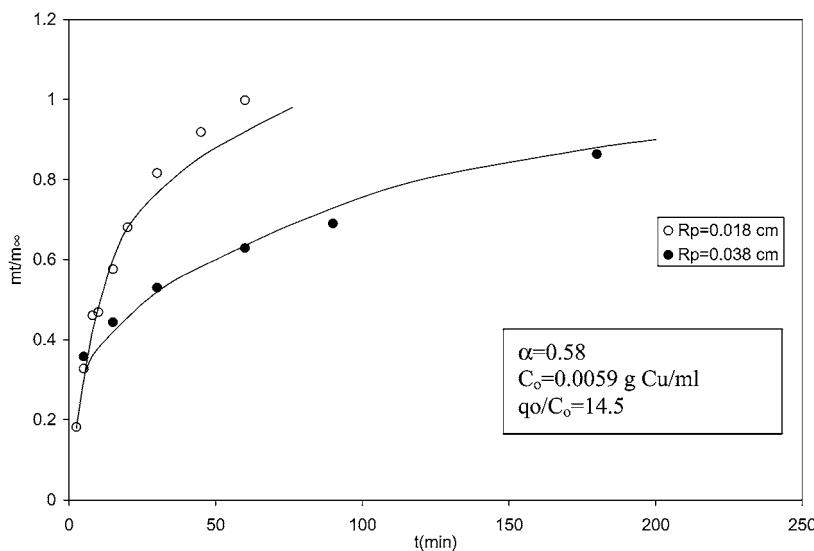


Figure 7. Uptake curves for runs 5 and 6 showing the comparison between the experimental curves and the theoretical curves calculated according to the shrinking core model Eq. (4) with the parameters given in Table 2.

Runs 5–7 were carried out at much higher concentration levels such that the isotherm may be regarded as approximately irreversible. The experimental conditions for runs 5 and 6 were not really comparable since both the concentration level and the value of α were different. Nevertheless the uptake curves, shown in Fig. 7 are broadly consistent in that the uptake rate is much higher for the smaller particles. The uptake

curves were analyzed using the shrinking core model for a finite volume system with the appropriate value of α (Eq. (4) or Fig. 3) and it may be seen from Table 1 that the resulting diffusivity values for both runs are similar.

Run 7 was carried out by sectioning individual particles and observing directly the advance of the concentration front, which is shown in Fig. 8 for two

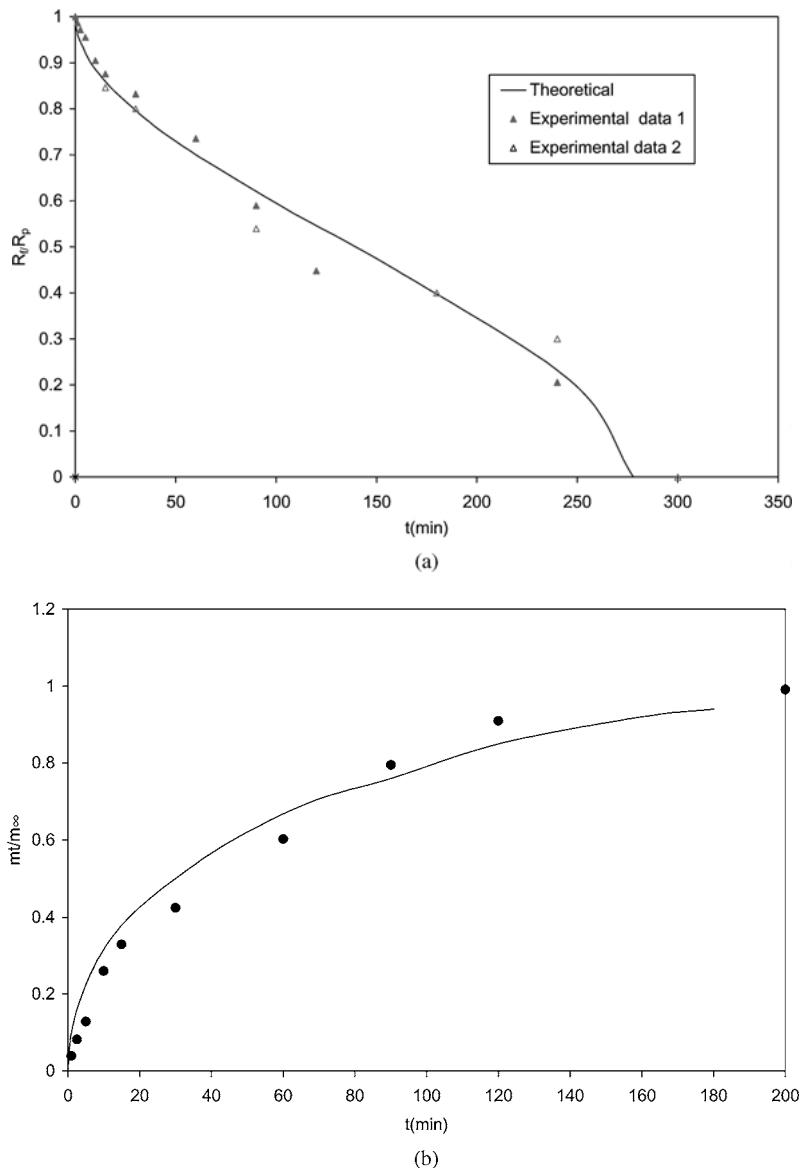


Figure 8. (a) Variation of r/R_p with time for single particle measurements (run 7). The theoretical curve is calculated from Eq. (5A) with the parameters given in Table 2. (b) Uptake curve for run 7 showing comparison between the experimental uptake estimated from the measurements of r/R_p and the theoretical curve calculated from Eq. (4) with the parameters given in Table 2.

replicate experiments. Also shown is the theoretical curve, calculated according to Eq. (5A) for $R_p^2 q_s / 6DC_0 = 278$ min (or $D_e/R_p^2 = 1.05 \times 10^{-5} \text{ cm}^2/\text{s}$). The corresponding uptake curve, calculated from the shrinking core measurements according to $m_t/m_\infty = 1 - z^3$ is shown in Fig. 8(b) together with the theoretical curve for $\alpha = 0$, $D_e/R_p^2 = 1.05 \times 10^{-5} \text{ cm}^2/\text{s}$. These curves evidently provide a good representation of the experimental data especially when it is remembered that the

measured particles were not all of precisely the same diameter.

For diffusion under linear conditions with a strongly adsorbed sorbate (K large) that is immobilized without obstructing the transport pores, $D_e \cong D/K$, where D represents the pore diffusivity. In the case of a rectangular isotherm the corresponding relationship is $D_e = DC_0/q_s$. Values of D calculated from these expressions are included in Table 2. It may be seen that for

runs 1 and 2 the value of D is about an order magnitude smaller than the molecular diffusivity which is consistent with the porosity of the resin with a normal tortuosity factor. In the presence of ammonia (runs 3 and 4) D is increased by a factor of 4 to a value ($2 \times 10^{-5} \text{ cm}^2/\text{s}$) which is in fact close to the value for the molecular diffusivity of CuSO_4 estimated from the Nernst equation ($1.7 \times 10^{-5} \text{ cm}^2/\text{s}$). This is a surprisingly large value and may suggest that the hydration layer of the Cu^{++} ion is significantly reduced in the presence of NH_3 , although we are not aware of any direct evidence of this. These values are similar to the diffusivities found by Rao et al. (1982) for diffusion of Pb and Cd in Dowex A-1 resin ($D \approx 10^{-5} \text{ cm}^2/\text{s}$). They also noted that their experimental diffusivities are close to the Nernst-Einstein prediction.

The diffusivities for runs 5–7 at substantially higher concentrations are about an order of magnitude smaller than for the low concentration (runs 1 and 2). A similar reduction of diffusivity with increasing concentration was also noted by Rao et al. (1982). The reason for this is not clear but may be related to swelling/contraction of the resin as a consequence of changes in the ionic strength of the solution.

Conclusions

The kinetic behavior of this system provides a good example of the transition from linear Fickian diffusional behavior at low concentration to irreversible (shrinking core) diffusional behavior at high concentrations. Diffusion control was confirmed by replicate measurements with different particle sizes. Despite the difference in the mathematical models the qualitative forms of the uptake curves for these two regimes are not very different (Ruthven, 2000). However shrinking core behavior was confirmed directly by sectioning individual resin particles exposed to the solution for different times.

Appendix: Derivation of Eq. (4)

Consider a volume V_s of adsorbent immersed in liquid of volume V_1 of initial concentration C_0 . The overall material balance is:

$$V[C_0 - C(t)] = V_s q \quad (1A)$$

Where $C(t)$ is the concentration in the solution at time t .

The balance for an individual particle is:

$$4\pi R^2 D \frac{\partial C}{\partial R} = \frac{4\pi D C(t)}{1/r - 1/R_p} = -4\pi r^2 q_s \frac{dr}{dt} \quad (2A)$$

Where $C(t)$ is given by Eq. (1A). The first term in Eq. (2A) represents the flux of sorbate through a surface of radius R in the region ($R_p > R > r$) see Fig. 2. The second term is obtained by integration from $c = C(t)$ at $R = R_p$ to $c = 0$ at $R = r$. The third term represents the advance of the shock front at radius r .

Since $q/q_s = 1 - z^3$, where $z = r/R_p$. Eq. (1A) may be written:

$$\frac{C(t)}{C_0} = 1 - \alpha + \alpha z^3 \quad (3A)$$

Substituting for $C(t)$ in Eq. (2A) and integrating yields:

$$\frac{DC_0 t}{R_p^2 q_s} = \int_{z=1}^z \frac{z(1-z)}{1-\alpha+\alpha z^3} dz \quad (4A)$$

which, since $m_t/m_\infty = 1 - z^3$, yields directly the uptake curve. For a system of infinite volume ($\alpha \rightarrow 0$) and Eq. (4A) becomes:

$$\frac{DC_0 t}{R_p^2 q_s} = \frac{1}{6} - \frac{1}{2}z^2 + \frac{1}{3}z^3 \quad (5A)$$

which is the familiar form for the shrinking core model for an infinite system.

Notation

b	Langmuir constant (Eq. (1))
c	Sorbate concentration within the pores of the polymer matrix
C_0	Initial concentration in solution
$C(t)$	Concentration in solution
C_f	Final value of $C(t)$
D_e	Effective diffusivity
m_t/m_∞	Fractional approach to equilibrium
q	Adsorbed phase concentration
q_s	Saturation limit (for Langmuir or irreversible isotherm)
q_f	Final value of q
q_n	Index (in Eq. (2))
r	Radius of concentration front in shrinking core model
R_p	Radius of particle

<i>R</i>	Radial coordinate
<i>t</i>	Time
<i>V</i> ₁	Volume of solution
<i>V</i> _s	Volume of solid adsorbent
<i>z</i>	(<i>r</i> / <i>R</i> _p) Dimensionless radial coordinate
α	Fraction of sorbate ultimately adsorbed = 1/ (1 + <i>V</i> ₁ / <i>KV</i> _s) for a linear system or <i>V</i> _s <i>q</i> _s / <i>V</i> ₁ <i>C</i> ₀ for irreversible case

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References

Crank, J. *The Mathematics of Diffusion*, p. 91, Oxford Press, London, 1956.

Gabai, B., N.A. dos Santos, D.C.S. Azevedo, S. Brandani, and C. Cavalcante, *Fundamentals of Adsorption*, vol. 6, pp. 1017–1022, Elsevier, Paris, 1998.

Radecki, P.R., J.C. Crittenden, D.R. Shonnard, and J.L. Bulloch, *Emerging Separation Technologies for Process Waste Reduction*, p. 51, AIChE, New York, 1999.

Rao, M.G., A.K. Gupta, E.S. Williams, and A.A. Aguwa, *AIChE Symposium Series*, **78**, 103–111 (1982).

Ruthven, D.M., “The Rectangular Isotherm Model for Adsorption Kinetics,” *Adsorption*, **6**, 287–291 (2000).

Suzuki, M., “Adsorption Engineering,” in *Chemical Engineering Monographs No. 25*, Kodansha-Elsevier Publishers, Tokyo, 1990.