SHORT PAPER

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A kinetic study of cadmium(II) adsorption on Lewatit TP260 resin

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Cadmium(II) adsorption from aqueous sulphate medium on Lewatit TP260 cationic (di-Na^+) ion exchange resin was investigated. The influence of operating variables such as aqueous pH, metal concentration, time and temperature on the equilibrium parameters was studied. Cadmium(II) adsorption on the resin can described by the Langmuir equation, whereas cadmium(II) uptake is particle diffusion controlled. The moving boundary particle diffusion model only fits the initial metal adsorption on the resin.

Keyword: Cadmium(II), Lewatit TP260 resin

Cadmium is obtained as by-product of zinc metallurgy being used in various industries, thus, it is also found in different wastes or residual materials. This metal has an important environmental impact due to its toxicity and, thus, its removal is a primary target. The removal of toxic metals, such as cadmium(II) by adsorption onto porous polymeric materials, *i.e.* ion exchange resins, is one of the broadly used methods for the detoxification of water and waste streams.[1,2]

In the present work, a kinetic study of cadmium(II) adsorption on Lewatit TP260 ion exchange resin is performed. The removal of cadmium(II) by the resin, the influence of pH, initial metal concentration, temperature, and contact time on the equilibrium parameters were also investigated.

Experimental

The investigation was carried out using the macroporous Lewatit TP260 ion exchange resin (Fluka), its typical properties being given in Table 1. The stock metal solution was prepared from cadmium sulphate (Baker). Working solutions were prepared from the stock solution by dilution with distilled water. The pH values of the solutions were adjusted by adding sulphuric acid or ammonia solutions. All chemicals were of AR grade.

The equilibrium adsorption of cadmium(II) on the resin under batch conditions was studied using 0.5 g resin samples and 200 mL of cadmium(II) aqueous solution of known concentration, adjusted to the required pH and temperature. After 3 h under continuous stirring (1200 min^{-1}) in a glass reactor vessel, the cadmium(II) concentration in the aqueous phase was determined by AAS. The continuous kinetic experiments were performed with 0.5 g resin which were treated with 200 ml solution containing known amounts of cadmium(II) at pH 6.0±0.05, 20°C and under constant stirring (1200 min^{-1}). Aliquots were taken periodically for AAS measurements of cadmium(II) concentration.

Results and discussion

The equilibrium adsorption of cadmium(II) by the resin from aqueous solutions at different initial pH values was measured. The results show that the metal adsorption by the resin increases sharply with an increase in pH between 2.0 and 4.0. Maximum cadmium(II) adsorption on the resin occurs at 4.0<pH<8.0 (20 mg cadmium/g resin).

The equilibrium adsorption of cadmium(II) by Lewatit TP260 resin was investigated at pH 6.0, 20°C and increasing amounts of cadmium(II) in the initial solution. The adsorption data were fitted to the two-parameter monolayer Langmuir isotherm. The linear Langmuir equation is written as:[3,4]

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \qquad (1)$$

where C_e represents metal concentration in solution at equilibrium (mg/l), X indicates the amount of metal adsorbed at equilibrium per unit mass of resin (mg/g), X_m denotes maximum adsorption capacity of resin (mg/g) and b denotes Langmuir constant related to binding energy (l/mg). The regression equation is represented by C_e/X=0.028+0.013C_e with r^2 (correlation coefficient) 0.999.

The values of the parameters X_m and b were determined as 76.9 mg/g and 0.46 l/mg, respectively. X_m is related with the accessibility of the adsorption sites inside the resin matrix and b reflects the binding strengths of fuctional groups with cadmium(II) ions.[5] The cadmium(II) adsorption is enhanced by an increase of the temperature (20–60°C range), thus the adsorption process is endothermic.

The adsorption of cadmium(II) on the resin from cadmium sulphate solutions at two different initial metal concentrations and pH 6.0±0.05 was studied as a function of time at 20°C. Experimental data are plotted as fractional attainment of equilibrium adsorption (F) versus time in Fig. 1. It is seen that the initial concentration of cadmium(II) has a slight effect on the rate of adsorption. The t_{50} values for 50% attainment of equilibrium adsorption are summarised in Table 2. The adsorption onto ion exchange resins must be considered as a liquid–solid phase reaction which includes several steps:[6]

i) the diffusion of ions from the solution to the resin surface,
ii) the diffusion of ions within the solid resin, and
iii) the chemical reaction between ions and functional groups (of the resin).

The adsorption of the metal is governed by the slowest of these processes.

The kinetic models and the rate equations for the above three cases have been established. The exchange Cd^{2+}–Na^+ can be described by the Nernst–Planck equations which apply to counter diffusion of two species in an almost homogeneous media.[7]

Table 1 Properties of Lewatit TP260 resin used for cadmium(II) adsorption

Polymer matrix	polystyrene-DVB
Functional group	(aminomethyl)phosphonic acid
Ionic form	di-Na^+
Particle size	0.4-1.25 mm
Ion exchange capacity	>2.3 (H^+) mequiv/ml

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

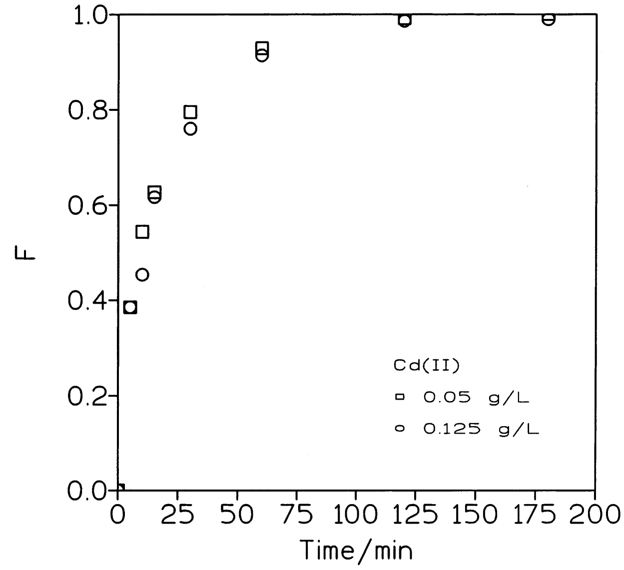

Fig.1 Rate of cadmium(II) adsorption on Lewatit TP260 resin.

Table 2 Kinetic parameters of cadmium(II) adsorption on Lewatit TP260 resin

Parameter	0.05 g/l Cd(II)	0.125 g/l Cd(II)
t_{50}, min	8	11
k, min^{-1}	3.3×0^{-2}	2.9×10^{-2}
D_r, cm^2/min	8.4×10^{-6}	7.3×10^{-6}

Table 3 The regression equations and regression coefficients (r^2, in parentheses)

Cadmium	Eqn(2)	Eqn(3)	Eqn(5)
0.05 g/l	y=0.041t (0.956)	y=0.033t (0.999)	y=0.011t (0.987)
0.125 g/l	y=0.038t (0.954)	y=0.029t (0.999)	y=0.010t (0.992)

If the liquid film diffusion controls the rate of exchange, the following relation can be used:

$$-\ln(1 - F) = kt \quad (2)$$

In the case of diffusion of ions in the resin phase controlling process, the equation used is:

$$-\ln(1 - F^2) = kt \quad (3)$$

in both Eqns (2) and (3), k is the kinetic coefficient or rate constant.

After testing both mathematical models proposed for homogeneous diffusion in the adsorption of cadmium(II) onto the resin, this is best fitted when the metal uptake is particle diffusion controlled (Table 3).

In Eqn (3), k is:

$$k = \frac{Dr\,\pi^2}{r_0^2} \quad (4)$$

where D_r is the diffusion coefficient in the resin phase and r_0 is the average radius of resin particle. Thus, the values of the adsorption rate constant and of the diffusion coefficient in the resin phase calculated from the slope of the straight lines (Fig. 2) are summarized in Table 2.

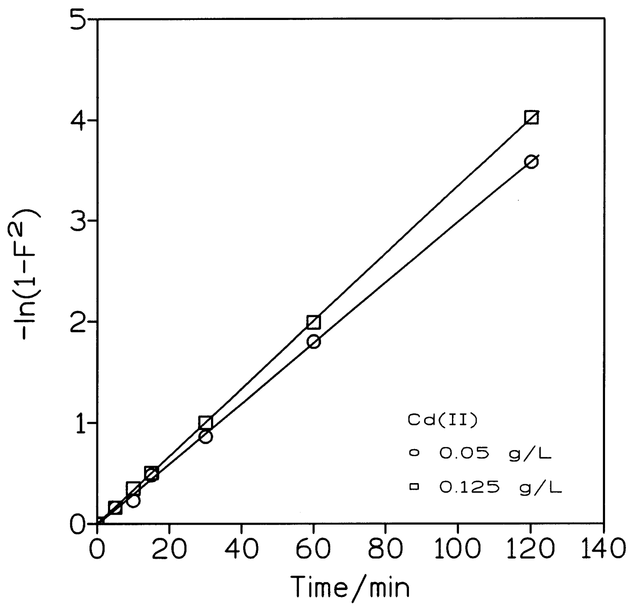

Fig.2 Plot of Eqn (3) for cadmium(II) adsorption on Lewatit TP260 resin.

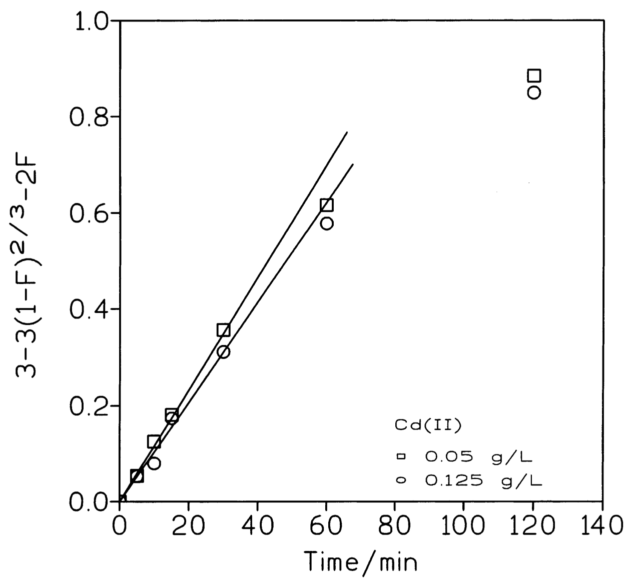

Fig.3 Plot of moving boundary particle diffusion model for the cadmium(II) adsorption on Lewatit TP260 resin.

When the adsorption of metal ion involves mass transfer accompanied by chemical reaction the process can be explained by the moving boundary model.[8] This model assumes a sharp boundary that separates a completely reacted shell from an unreacted core and that advances from the surface toward the center of the solid with the progression of adsorption. In this case, the rate equation is given by:

$$3 - 3(1 - F)^{\frac{2}{3}} - 2F = kt \quad (5)$$

The graphical correlation in Fig. 3 of $3–3(1–F)^{2/3}–2F$ versus t shows that the moving boundary particle diffusion model fits only the initial adsorption on the Lewatit TP260 resin. The linear regression analysis of functions $3–3(1–F)^{2/3}–2F$ versus time are also given in Table 3.

Conclusions

The results on the present study indicate that the adsorption of cadmium(II) from sulphate medium onto the Lewatit TP260 reaches a maximum between pH values of 4.0 and 8.0. The adsorption can be described by the Langmuir isotherm, with X_m and b parameters estimated as 76.9 mg/g and 0.46 l/mg respectively. The cadmium(II) uptake is best explained by a particle diffusion controlled process, whereas the moving boundary model only fits the initial cadmium(II) adsorption on the resin.

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References

1 N.M. Lee and C.Y. Liu, *J. Chin. Chem. Soc.*, 1995, **42,** 521.
2 M. Streat, *Ind. Eng. Chem. Res.*, 1995, **34,** 2481.
3 K. Periasamy and C. Namasivayam, *Ind. Eng. Chem. Res.*, 1994, **33,** 317.
4 R.N. Sahoo, S.C. Das, B.R. Reddy, P.C. Rath and R.P. Das, *Hydrometallurgy*, 2001, **62,**185.
5 W. Lin and Y.L. Hsieh, *J. Polym. Sci.: Part A*, 1997, **35,**631.
6 F. Helfferich, In: *Ion Exchange*, vol.1, J.A. Marinsky (ed.), Marcel Dekker, NY, 1966.
7 R. Chiarizia, E.P. Horwitz and S.D. Alexandratos, *Solvent Extr. Ion Exch.*, 1994, **12,** 211.
8. M. Chanda and G.L. Rempel, *Ind. Eng. Chem. Res.*, 1994, **33,** 623.