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Ion-exchange kinetics of Cu(II) and Zn(II) from aqueous solutions with two chelating resins

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Abstract

The Na form of two chelating ion exchange resins Chelex 100 (Bio-Rad) and Amberlite IRC 748, both of which have iminodiacetic acid function group, was used to exchange Cu^{2+} and Zn^{2+} from aqueous solutions. Kinetic experiments were performed at 298 K in a batch mode by varying the initial concentration of metal ions (3–9 mol/m^3) and initial aqueous pH value (2.0–6.5). The kinetic data were first treated by conventional unreacted-core model and by the Fick's first law that takes into account diffusion of metal ions within resin pores. The effective diffusion coefficients of metal ions were evaluated. The kinetic data were also treated and compared by a second-order reversible reaction model based on exchange reaction equilibrium. It was shown that the rate constants for Cu^{2+} and Zn^{2+} exchange with Amberlite IRC 748 resin were larger than with Chelex 100 resin under comparable conditions.

Keywords: Ion exchange kinetics; Heavy metals; Chelating resins; Unreacted-core model; Pore diffusion model; Reversible reaction model

1. Introduction

In many industries such as mining, metal plating, tanning, and nuclear power plant operations, there are always serious heavy metal contaminations existing in the discharged wastewaters [1]. There is a risk that the surrounding soils as well as the ground and surface waters are contaminated by metal-containing effluents. Thus, to remove the hazardous heavy metals from industrial wastewaters is the major course that cannot be ignored. For years, many methods have been developed to remove heavy metals from the effluents including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, and adsorption on several low-cost adsorbents such as activated carbons [1–6]. Chemical precipitation is the most conventional method; however, it is hard to handle a large volume of the wastewater containing relatively low concentration of heavy metals. Alternatively, ion exchange is the effective and common one for this purpose because the resins can be easily recovered and reused by regeneration operation [4,5].

On the other hand, ion exchange resins with specific functional groups like iminodiacetic acid (IDA), aminophosphonic acid, and amidoxime, as commonly referred to the chelating resins, have been widely used to recover heavy metals from wastewaters [4,6,7]. They are very powerful because the functional groups can form coordination bonds with many heavy metals. It is often that just one kind of heavy metals, particularly transition metals, is selectively removed from wastewater [8–10]. A most common type of chelating resins like Chelex 100, Ambelite IRC 748, Purolite S930, and Lewatit TP 207, all which contains IDA group, has been extensively applied for the recovery of heavy metal ions including Ni^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, and Cr^{3+} from aqueous solutions [4,5,7–20]. This is because IDA group could provide electron pairs so that the binding forces for alkaline earth metals is 5000 times than those for alkali metals like Na^{+}, which react with divalent metals to form a stable coordination covalent bond. For example, Chelex 100 and IRC 718 resins have been employed to treat the effluents discharged from printed circuit board manufacturing, which contain Cu^{2+}, Ni^{2+}, Na^{+}, and some complexing ligands such as EDTA and citrate [14,15]. Korngold et al. [16] also removed Cu^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+} from tap water containing small amounts of salts of carboxylic acid using Purolite S930 resin. They found that the presence of one carboxylic group salts like acetate has little effect on exchange performance. The presence of salts with two or four carboxylic groups such as tartrate and EDTA dramatically decreases the exchange efficiency.

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Nomenclature

D_M	effective diffusion coefficient of metal ions within the resin particle (m^2/s)
f	exchange conversion of the resin defined in Eq. (2)
k	rate constant defined in Eq. (15) (s^{-1})
k_b	backward reaction rate constant defined in Eq. (10) ($m^6/mol^2\ s$)
k_f	forward reaction rate constant defined in Eq. (10) ($m^3/mol\ s$)
$K_{M\text{–}Na}$	exchange equilibrium constant defined in Eq. (12) (mol/m^3)
m_i	amount of species i present in the resin (mol/m^3 of resin)
q_e	equilibrium amount of metal exchanged at a given pH and metal concentration (mol/m^3 of resin)
q_t	amount of metal exchanged at any time at a given pH and metal concentration (mol/m^3 of resin)
q_{sat}	exchange capacity of the resin at a given pH (mol/m^3 of resin)
r_c	radius of the interface of unreacted core (m)
r_0	radius of the resin (m)
R^2	correlation coefficient
t	time (s)
V	volume of the solution (m^3)
W	weight of dry resins (kg)

Greek letters

ρ_s	density of dried resin particle (kg/m^3)
τ	time required for reaching reaction equilibrium (s)

Subscript

0	initial

Ion exchange processes are generally operated in fixed beds (columns) in practical applications [21,22]. If we want to know what kind or concentration of metal ions exits a resin column at what time period in the future, we need to understand the dynamic phenomena of the columns. That is, batch ion exchange kinetics should be investigated. Some kinetic models such as the Nernst–Planck equation have been satisfactorily applied to describe the exchange process [23]; however, the mathematical complexity of such models makes them inconvenient to follow in practice. Therefore, a simplified but reasonably adequate kinetic model was proposed and screened in this work.

A resin particle can be regarded as an ensemble of microspheres with pores inside them; pore diffusion model (PDM) is satisfactory for describing intraparticle mass transfer within such porous structures [4,23,24]. There are two classes of kinetic models can be utilized, the first includes the PDM and isotopic exchanged model, and the other includes the shrinking-core, shell-progressive or unreacted-core model (UCM), and the "progressive conversion" model [4]. Here, the ion exchange kinetics of Cu^{2+} and Zn^{2+} with Na-form Chelex 100 and Amberlite IRC 748 resins in a batch mode was systematically studied. Experiments were performed at 298 K and different initial metal concentrations (3–9 mol/m^3) and aqueous pH values (2.0–6.5). The evolution of intraparticle profiles was measured by microscopic techniques to make discrimination between the PDM and UCM, and the effective diffusion coefficients were evaluated.

2. Materials and methods

2.1. Resins and solutions

Two chelating resins Chelex 100 (Sigma Co.) and Amberlite IRC 748 (Rohm Haas Co.) were used and compared because they both contain IDA functional groups. The physical properties and specification as reported by the manufacturers are listed in Table 1. These resins were washed with NaOH (1 mol/dm^3), HCl (1 mol/dm^3), and *n*-hexane to remove possible organic and inorganic impurities. They were then washed with deionized water (Millipore Milli-Q) three times, and were converted to Na^+ form by column flushing with 1 mol/dm^3 NaCl for 12 h [11]. These resins were finally washed with deionized water and dried in vacuum oven at 333 K.

Analytical-reagent grade of $Cu(NO_3)_2$, $Zn(NO_3)_2$, and other inorganic chemicals including NaCl, HCl, NaOH, and HNO_3 were purchased from Merck Co. The aqueous solution was prepared by dissolving metal nitrate in deionized water, and the initial concentrations were in the range 3–9 mol/m^3. When the effect of aqueous pH on the exchange was studied, the initial pH values of Cu^{2+} and Zn^{2+} solutions were adjusted to be in

Table 1
Physical and chemical properties of the chelating resins used

Properties	Chelex 100	Amberlite IRC 748
Grade	Laboratory grade	Industrial grade
Physical form	Small, white beads	Opaque, beige beads
Functional group	Iminodiacetic acid	Iminodiacetic acid
Matrix	Styrene–divinylbenzene	Styrene–divinylbenzene
Structure	Macroporous	Macroporous
Particle size (mm, dry)	0.15–0.30 (50–100 mesh)	0.50–0.65
Capacity (equiv./m^3 of resin)	700	1250
Bulk density ρ_s (kg/m^3)	968	687
pH range	0–14	1.5–14
Maximum operating temperature	75 °C (Na^+ form)	90 °C (Na^+ form)

the ranges 2.0–4.5 and 2.5–6.5, respectively (Mettler digital pH meter MP 220) by adding a small amount of 0.1 mol/dm^3 HNO_3 or NaOH. Under those pH ranges tested, the precipitation of Cu^{2+} and Zn^{2+} hydroxides in aqueous solutions could be avoided.

2.2. Experimental procedures

The exchange kinetic experiments were carried out in a Pyrex glass vessel of 100 mm i.d. and 130 mm height, fitted with four glass baffles, 10 mm width. An aqueous solution (0.6 dm^3) was poured and agitated using a Cole-Parmer Servodyne agitator wit six blades, flat-bladed impeller (12 mm height, 40 mm width). The stirring speed was 500 rpm since above that the agitation has little effect on ion exchange. In addition, the resins could be well suspended in the solution at this stirring speed. An amount of dry resin (1.8 g) was then added into the vessel and the timing was started. The whole vessel was immersed in a water bath at 298 K (Haake K-F3, Germany).

At preset time intervals, the samples (1 cm^3) were withdrawn after 0.45 μm Whatman membrane filters, and the concentrations of metals were analyzed with a Perkin-Elmer atomic absorption spectrophotometer (AA-100). The amount of metal exchanged at any time t, q_t (mol/m^3 of resin), was thus calculated by:

$$q_t = \frac{(C_{\mathrm{M},0} - C_{\mathrm{M}})V}{W/\rho_{\mathrm{s}}} \qquad (1)$$

where $C_{\mathrm{M},0}$ and C_{M} are the aqueous-phase concentrations of metals at the initial and any time t, respectively (mol/m^3), V the volume of aqueous solution (0.6 dm^3), W the weight of dry resin used (1.8 g), and ρ_{s} is the density of dried resin (kg/m^3). Each experiment was at least duplicated under identical conditions. The reproducibility of the measurements was within 4%.

3. Results and discussion

3.1. Effect of initial pH on exchange kinetics

Figs. 1 and 2 show the typical time profiles during the exchange of Cu^{2+} and Zn^{2+} with two Na-form chelating resins. Under those pH values, the amounts of Cu^{2+} and Zn^{2+} exchanged increase with increasing pH values. That is, the optimal pH will be around 4.5 and 6.5 for Cu^{2+} and Zn^{2+}, respectively.

It is found that the concentrations of Cu^{2+} and Zn^{2+} in aqueous solutions decrease more rapidly in the early stage of operation (50–100 min), and the exchange is virtually completed within 150–200 min. That is, the decrease of the concentrations of Cu^{2+} and Zn^{2+} in the solution demonstrates that higher exchange rates (dC_{M}/dt) of Cu^{2+} and Zn^{2+} with Na-form chelating resins are obtained at the onset; and the plateau is reached gradually within 50 min. Regardless of the use of IRC 748 or Chelex 100 resin, it is observed from kinetic experiments that the amount of Cu^{2+} exchanged is larger than that of Zn^{2+} exchanged, as reported from our previous equilibrium results [12].

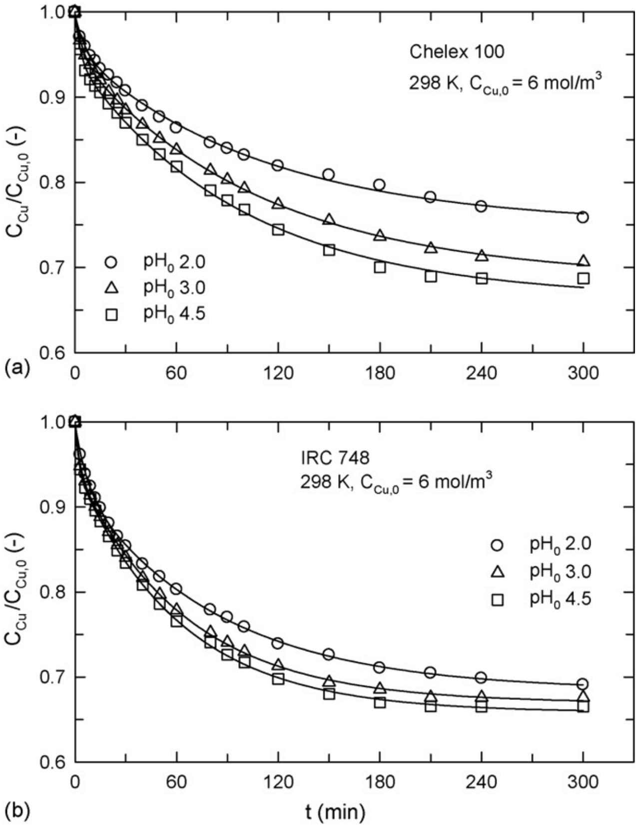

Fig. 1. Time profiles for the exchange of 6 mol/m^3 Cu^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

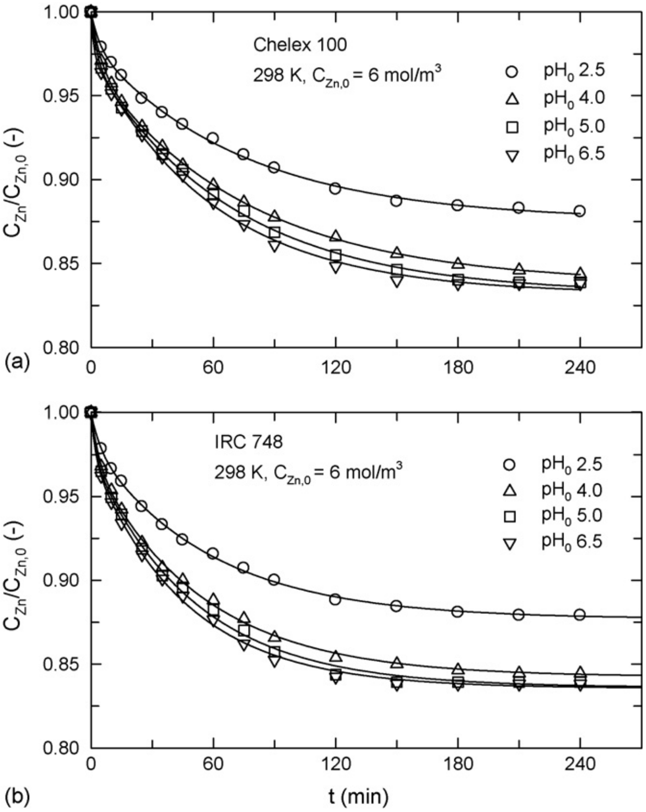

Fig. 2. Time profiles for the exchange of 6 mol/m^3 Zn^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

3.2. Unreacted-core model

In formulating the unreacted-core model, we proceed from the following assumptions. Let us consider a spherical particle surrounded by an external solution of constant concentration. Resin particles are composed of two phases: a solid porous matrix where ion exchange occurs and pores filled with an inner solution. When metal ions are exchanged with the resins, initially, the exchange reaction is only carried out on the surface of the resin, and as the time passed the reaction sites are gradually moved to the interior of resin particles. This type of heterogeneous diffusion process can be described by UCM [23,25]. The UCM, when diffusion through the reacted shell, is the rate-controlling step (i.e., the reaction rate is fast compared with the diffusion rate).

Assuming a quasi-steady state the exchange conversion (*f*), which is defined as the ratio of the amount of metal exchanged at any time to that at equilibrium, can be described by the following equation:

$$1 - f = \frac{\text{volume of unreacted particle}}{\text{total volume of particle}} = \frac{(4/3)\pi r_c^3}{(4/3)\pi r_0^3} = \left(\frac{r_c}{r_0}\right)^3 \tag{2}$$

where r_0 is the initial radius of resin particle and r_c is the radius of the interface of unreacted core. Here, r_c is difficult to determine from experiments, so we alternatively use the exchange conversion (*f*) to represent this quantity.

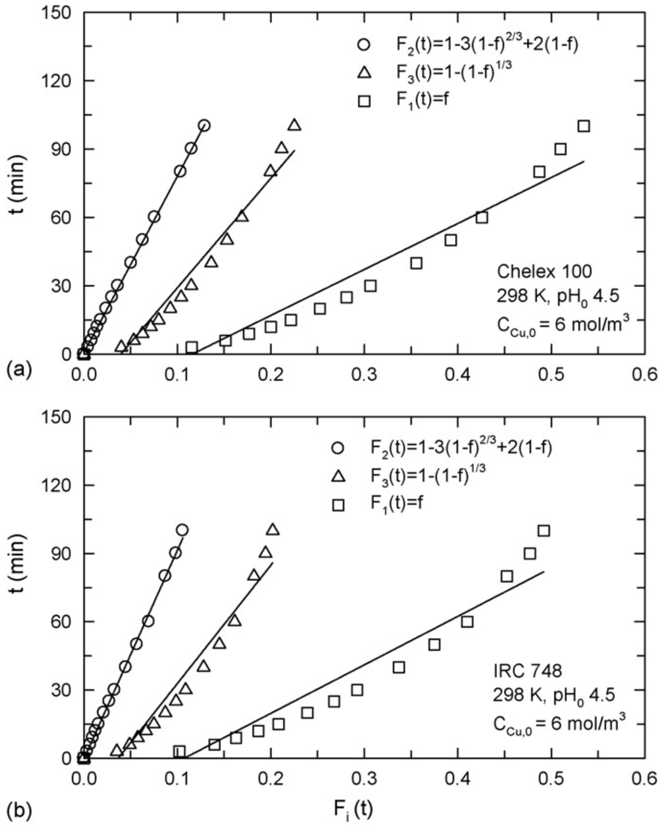

Fig. 3. The unreacted-core model for the exchange of 6 mol/m^3 Cu^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

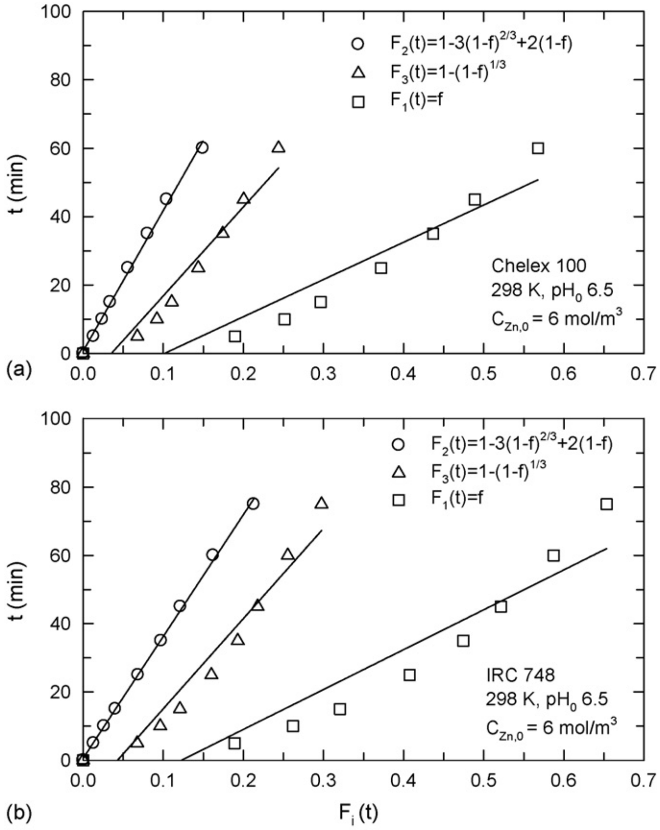

Fig. 4. The unreacted-core model for the exchange of 6 mol/m^3 Zn^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

In this model, the components surface or solid-phase diffusion is assumed to be negligible (infinite bath). In fact, the exchange of ions by the resins from aqueous solution has been thoroughly treated [21,26]. Ion exchange process can be limited by (i) diffusion through a boundary film around the resin particle (film diffusion), (ii) diffusion within the resin particle (intraparticle diffusion), and (iii) exchange reaction. If diffusion within the resin particle is limiting, the following relationship can be obtained [23].

$$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{r_0}\right)^2 + 2\left(\frac{r_c}{r_0}\right)^3 \tag{3}$$

or

$$F_2(t) = \frac{t}{\tau} = 1 - 3(1-f)^{2/3} + 2(1-f) \tag{4}$$

where τ is the time required for complete conversion of the resin particle from Na form to the Cu or Zn form. In the cases where film diffusion or exchange reaction is the rate-controlling step, Eq. (4) would be replaced by $F_1(t) = f$ and $F_3(t) = 1 - (1-f)^{1/3}$, respectively [23].

Figs. 3 and 4 show the results for the exchange of Cu^{2+} and Zn^{2+} with two chelating resins. A good linearity is obtained only for the plots of $F_2(t)$ against t (correlation coefficient $R^2 > 0.9962$, Table 2). This is all the case no matter what Cu^{2+} or Zn^{2+} is exchanged with Chelex 100 or IRC 748 resin. Although the UCM is applicable in these exchange systems, the parameter τ strongly depends on aqueous pH value and metal concentra-

Table 2
The unreacted-core model for the exchange of Cu^{2+} and Zn^{2+} with Na-form chelating resins at 298 K

System	$C_{M,0}$ (mol/m^3)	pH$_0$	$F_1(t)$		$F_2(t)$		$F_3(t)$	
			τ (s)	R^2	τ (s)	R^2	τ (s)	R^2
Cu-Chelex 100	6	2.0	208	0.8951	888	0.9976	507	0.9316
		3.0	203	0.9110	802	0.9997	486	0.9474
		4.5	202	0.9132	774	0.9995	480	0.9501
Cu-Chelex 100	9	2.0	145	0.8831	550	0.9992	346	0.9312
		3.0	144	0.8891	533	0.9991	342	0.9371
		4.5	143	0.8892	512	0.9985	337	0.9388
Cu-IRC 748	6	2.0	213	0.8856	969	0.9970	526	0.9224
		3.0	213	0.8999	929	0.9988	522	0.9351
		4.5	213	0.9014	917	0.9981	520	0.9365
Cu-IRC 748	9	2.0	147	0.8733	584	0.9992	354	0.9216
		3.0	144	0.8826	543	0.9999	344	0.9317
		4.5	143	0.8942	522	0.9993	337	0.9411
Zn-Chelex 100	3	2.0	176	0.8985	1293	0.9985	468	0.9222
		4.0	159	0.9036	996	0.9978	415	0.9316
		6.5	153	0.9000	903	0.9966	396	0.9305
Zn-Chelex 100	6	2.0	124	0.8921	588	0.9985	309	0.9291
		4.0	112	0.8881	447	0.9986	270	0.9345
		6.5	109	0.8901	411	0.9962	260	0.9387
Zn-IRC 748	3	2.0	171	0.8986	895	0.9992	434	0.9311
		4.0	167	0.8933	837	0.9997	420	0.9287
		6.5	165	0.8854	813	0.9994	415	0.9235
Zn-IRC 748	6	2.0	120	0.8952	396	0.9983	277	0.9445
		4.0	117	0.8782	365	0.9978	265	0.9358
		6.5	117	0.8826	357	0.9989	264	0.9417

tion. This makes the UCM inconvenient to apply in modeling fixed-bed operations.

3.3. Pore diffusion model

Model equations include a mass balance for species i in a volume element and of the particle, with the associated boundary and initial conditions. The main assumptions made are that (i) film diffusion around the resin particles is negligible and (ii) the effective diffusion coefficient for binary ion exchange is constant [21,23]. The phenomenon is described by the Fick's first law of diffusion. By the relationship between the decreasing rate of ion exchange in the solution and the radius r_c of interface of the unreacted core, we have:

$$V\frac{\mathrm{d}C_M}{\mathrm{d}t} = 4\pi q_{sat} r_c^2 \frac{\mathrm{d}r}{\mathrm{d}t} = 4\pi D_M\left[\frac{1}{(1/r_0)-(1/r_c)}\right] C_M \qquad (5)$$

where D_M is the effective diffusion coefficient of metal ion within the resin (m^2/s) and q_{sat} is the exchange capacity of the resin at a given pH (mol/m^3 of resin). Eq. (5) can be rearranged into,

$$q_{sat}\int_{r_0}^{r_c}\left(\frac{1}{r_0}-\frac{1}{r_c}\right) r_c^2\,\mathrm{d}r = D_M\int_0^t C_M\,\mathrm{d}t \qquad (6)$$

Integrating and combining with Eq. (4), we can obtain,

$$F_2(t) = 1-3(1-f)^{2/3}+2(1-f) = \frac{6D_M C_{M,0}}{q_{sat} r_0^2}\int_0^t\left(\frac{C_M}{C_{M,0}}\right)\mathrm{d}t = \left(\frac{6D_M C_{M,0}}{q_{sat} r_0^2}\right) Y(t) \qquad (7)$$

and

$$f = \frac{C_{M,0}V_0-(C_{M,n}V_n+\sum_{i=1}^{n}C_{M,i}V_i)}{Wq_{sat}/\rho_s} \qquad (8)$$

where $C_{M,0}$, V_0, $C_{M,n}$, and V_n are the metal concentrations and volumes of the solution at the initial and any time t, respectively; $C_{M,i}$ and V_i are the metal concentration and volume of the solution taken at the ith sampling.

While $F_2(t)$ is plotted versus $Y(t)$ (using the Simpson's method, $R^2 > 0.9932$), as shown in Figs. 5 and 6, we can calculate the effective diffusion coefficients D_M (Table 3). At 298 K, the D_M values for Cu(II) with Chelex 100 and IRC 748 resins are obtained to be 2.5×10^{-11} and 1.5×10^{-10} m^2/s, respectively, whereas those of Zn(II) with Chelex 100 and IRC 748 resins are 2.0×10^{-11} and 1.2×10^{-10} m^2/s, respectively. Those coefficients in the order 10^{-10} to 10^{-11} m^2/s are essentially comparable to the literature results [21–23]. Interestingly, the industrial-grade IRC 748 resins provide about one order of magnitude larger D_M than the laboratory-grade Chelex 100 resins.

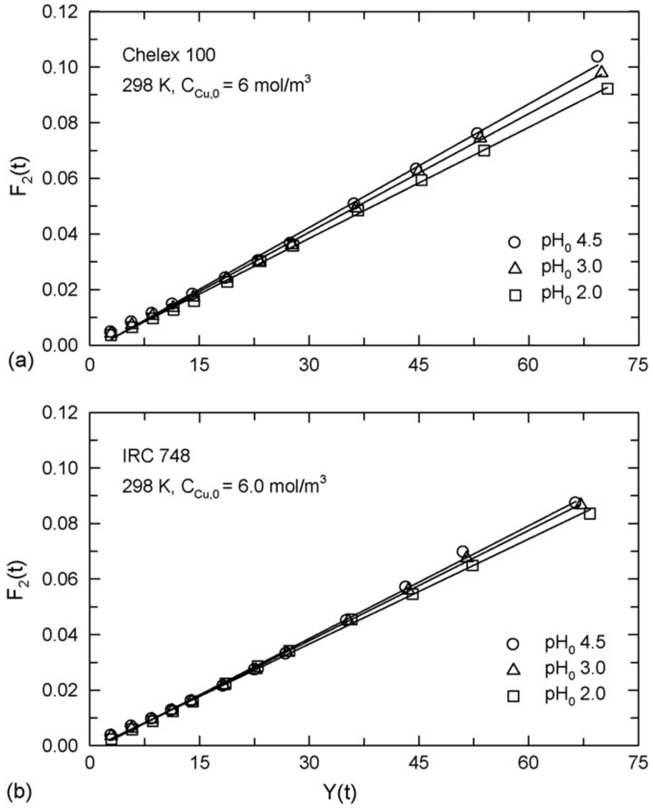

Fig. 5. The pore diffusion model for the exchange of 6 mol/m^3 Cu^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

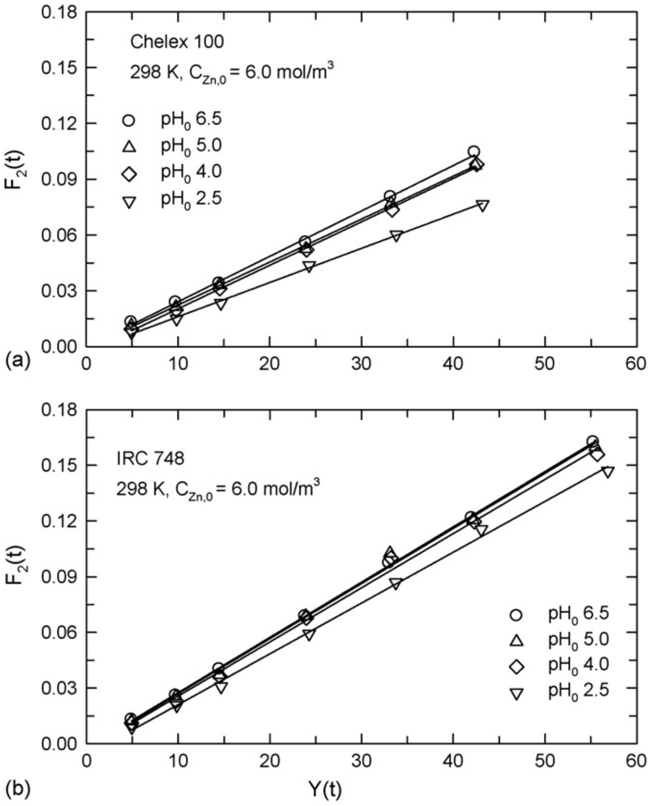

Fig. 6. The pore diffusion model for the exchange of 6 mol/m^3 Zn^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

Table 3
The effective diffusion coefficients for the exchange of Cu^{2+} and Zn^{2+} with Na-form chelating resins at 298 K

System	$C_{M,0}$ (mol/m^3)	pH$_0$	$(6D_M C_{M,0})/(q_{sat} r_0^2)$ (s^{-1})	q_{sat} (mol/m^3)	D_M (m^2/s)
Cu-Chelex 100	6	4.5	0.00148	794	2.66×10^{-11}
		3.0	0.00142	784	2.52×10^{-11}
		2.0	0.00133	743	2.23×10^{-11}
Cu-Chelex 100	9	4.5	0.00220	800	2.70×10^{-11}
		3.0	0.00209	792	2.54×10^{-11}
		2.0	0.00201	751	2.30×10^{-11}
Cu-IRC 748	6	4.5	0.00135	763	1.58×10^{-10}
		3.0	0.00132	746	1.50×10^{-10}
		2.0	0.00126	692	1.31×10^{-10}
Cu-IRC 748	9	4.5	0.00221	724	1.64×10^{-10}
		3.0	0.00211	706	1.52×10^{-10}
		2.0	0.00194	678	1.34×10^{-10}
Zn-Chelex 100	3	6.5	0.00115	392	2.05×10^{-11}
		5.0	0.00105	396	1.90×10^{-11}
		4.0	0.00101	385	1.75×10^{-11}
Zn-Chelex 100	6	6.5	0.00244	391	2.16×10^{-11}
		5.0	0.00231	390	2.04×10^{-11}
		4.0	0.00234	379	2.00×10^{-11}
Zn-IRC 748	3	6.5	0.00138	304	1.28×10^{-10}
		5.0	0.00135	298	1.23×10^{-10}
		4.0	0.00133	288	1.17×10^{-10}
Zn-IRC 748	6	6.5	0.00298	291	1.32×10^{-10}
		5.0	0.00297	277	1.26×10^{-10}
		4.0	0.00292	270	1.20×10^{-10}

However, the same concern as UCM is present in PDM because the parameters q_{sat} and D_M depend on aqueous pH value and/or metal concentration.

3.4. Second-order reversible reaction model

If an ion exchange resin is considered as a charged adsorbent, it is possible that the monolayer coverage of metal ions on the surface of the adsorbent is formed because the exchange reaction is essentially a kind of chemical reaction [18,27,28]. The exchange reaction of divalent metals (M^{2+}) with the Na-form Chelex 100 and IRC 748 resins (RNa_2) can be represented as [11–13,19]:

$$RNa_2(s) + M^{2+}(aq) \Leftrightarrow RM(s) + 2Na^+(aq), \quad k_f/k_b \tag{9}$$

where *R* refers to the resin matrix.

It is established that the exchange of metal ions on heterogeneous surface is a second-order reversible kinetics. There are two important physicochemical aspects for parameter evaluation in the exchange process, i.e., kinetics and equilibrium. Therefore, the rate of exchange can be given by:

$$\frac{dq_t}{dt} = k_f m_{RNa_2} C_M - k_b C_{Na}^2 q_t \tag{10}$$

where m_{RNa_2} is the amount of Na present in the resin (mol/m^3 of resin), k_f the forward reaction rate constant (m^3/mol s), and k_b is the backward reaction rate constant (m^6/mol^2 s). For simplicity, then the reaction rate becomes [7,29]

$$\frac{dq_t}{dt} = k_f m_{RNa_2}(C_{M,0} - q_t) - k_b C_{Na}^2 q_t = k_f'(C_{M,0} - q_t) - k_b' q_t \tag{11}$$

The rate constants of k_f and k_b can be related to the equilibrium constant of Eq. (9) $K_{M\text{–}Na}$ as follows [12,19,29].

$$K_{M\text{–}Na} = \frac{k_f}{k_b} = \frac{q_e C_{Na}^2}{m_{RNa_2} C_M} = \frac{k_f'}{k_b'}\left(\frac{C_{Na}^2}{m_{RNa_2}}\right) \tag{12}$$

where q_e represents the equilibrium amount of metal exchanged at a given initial aqueous pH and metal concentration (mol/m^3 of resin). It was found that the $K_{M\text{–}Na}$ value decreases with increasing ionic strength of aqueous solution [12]. Under the restricted ranges of metal concentration tested (3–9 mol/m^3), however, $K_{M\text{–}Na}$ can be treated to be nearly constant.

When the exchange process approaches equilibrium, Eq. (13) can be obtained from Eq. (11).

$$\frac{dq_t}{dt} = k_f'(C_{M,0} - q_e) - k_b' q_e = 0 \tag{13}$$

Combining Eqs. (11) and (13), we have [7]

$$\ln\left(1 - \frac{q_t}{q_e}\right) = \ln(1 - f) = -(k_f' + k_b')t = -kt \tag{14}$$

where *f* is the exchange conversion of the resin (=q_t/q_e), and

$$k = k_f' + k_b' = k_f m_{RNa_2} + k_b C_{Na}^2 \tag{15}$$

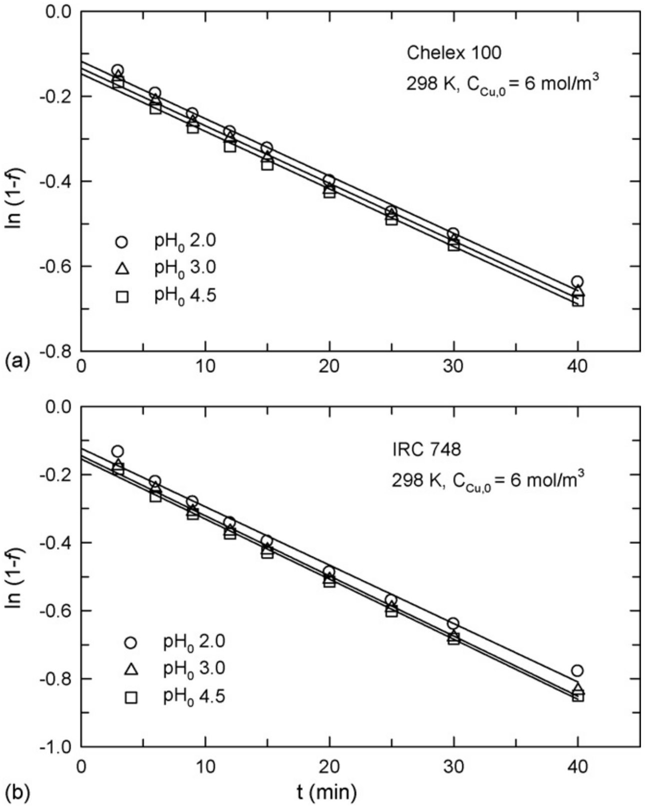

Fig. 7. The second-order reversible reaction model for the exchange of 6 mol/m^3 Cu^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

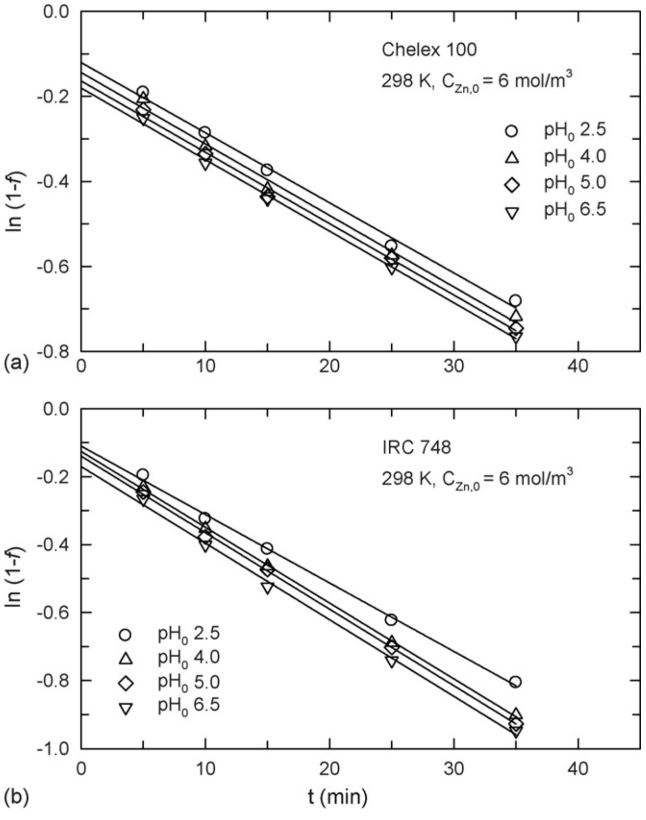

Fig. 8. The second-order reversible reaction model for the exchange of 6 mol/m^3 Zn^{2+} with Na-form Chelex 100 and IRC 748 resins at 298 K.

Table 4
Parameters of second-order reversible reaction model for the exchange of Cu^{2+} and Zn^{2+} with Na-form chelating resins at 298 K

System	$C_{M,0}$ (mol/m^3)	$K_{M\text{–}Na}$ (mol/m^3)	k (s^{-1})	k_f (m^3/mol s)	k_b (m^6/mol^2 s)
Cu-Chelex 100	6	6.47	0.0135	7.74×10^{-3}	1.20×10^{-3}
	9	6.46	0.0164	7.74×10^{-3}	1.20×10^{-3}
Cu-IRC 748	6	8.54	0.0175	8.20×10^{-3}	0.96×10^{-3}
	9	8.53	0.0235	8.30×10^{-3}	0.97×10^{-3}
Zn-Chelex 100	3	0.25	0.0108	2.65×10^{-3}	1.07×10^{-2}
	6	0.25	0.0167	2.59×10^{-3}	1.04×10^{-2}
Zn-IRC 748	3	0.42	0.0133	2.71×10^{-3}	6.41×10^{-2}
	6	0.42	0.0219	2.68×10^{-3}	6.33×10^{-2}

Figs. 7 and 8 show the good linearity in the plots of $\ln(1-f)$ against t for the exchange of Cu^{2+} and Zn^{2+} with two chelating resins ($R^2 > 0.9956$). The calculated values of k, k_f, and k_b are listed in Table 4. It is found that the rate constant, particularly for k_f, remains nearly unchanged although the initial metal concentration varies. This likely verifies the validity of this second-order reversible reaction model. Moreover, the forward rate constant of Cu^{2+} is about three times larger than that of Zn^{2+} no matter what Chelex 100 or IRC 748 is used; but the backward rate constant of Zn^{2+} is much larger than that of Cu^{2+}. Thus, the exchange capacity of Zn^{2+} with both chelating resins is less than that of Cu^{2+}, as shown in Figs. 1 and 2. Evidently, this reversible reaction model gives satisfactory but more unified results because its parameters such as k_f and k_b do not essentially depend on the aqueous pH and metal concentration.

4. Conclusions

Three simplified kinetic models (the unreacted-core model, pore diffusion model, and second-order reversible reaction model) have been tried in this work to follow the exchange kinetics of Cu^{2+} and Zn^{2+} with the Na-form Chelex 100 and Amberlite IRC 748 resins at 298 K. Although the easy-to-follow unreacted-core model and pore diffusion model (both with the characteristics of intraparticle diffusion) revealed excellent description of kinetic data, the model parameters always depended of solution environments (e.g., aqueous pH and metal concentration in this case). This makes them rather inconvenient to apply in an extended range of operation conditions. The second-order reversible reaction model, which is based on mass-action law and reaction equilibrium relationship, also yielded a good fit for the kinetic data; however, this model was suggested for the subsequent modeling of column operation because its parameters such as the forward and backward rate constants (k_f and k_b) did not change with aqueous pH and metal concentration, at least under the ranges studied.

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References

[1] J.W. Pattersom, Wastewater Treatment Technology, Ann Arbor Science Pub. Inc., Ann Arbor, MI, 1985, pp. 199–215.

[2] T. Mohammadi, A. Moheb, M. Sadrzadeh, A. Razmi, Modeling of metal ion removal from wastewater by electrodialysis, Sep. Purif. Technol. 41 (2005) 73–82.

[3] Z. Ujang, G.K. Anderson, Performance of low-pressure reverse osmosis membrane for separating mono- and divalent ions, Water Sci. Technol. 38 (4–5) (1998) 521–528.

[4] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Selective removal of heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2004) 91–106.

[5] W. Fries, D. Chew, Get the metal out, Chemtech 23 (2) (1993) 32–35.

[6] H. Eccles, H. Greenwood, Chelate ion-exchangers: the past and future application, a user's view, Solvent Extr. Ion Exch. 10 (1992) 713–727.

[7] S. Rengaraj, S.H. Moon, Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins, Water Res. 36 (2002) 1783–1793.

[8] J. Yang, A. Renken, Heavy metal adsorption to a chelating resin in a binary solid fluidized bed, Chem. Eng. Technol. 23 (2000) 1007–1012.

[9] M.E. Malla, M.B. Alvarez, D.A. Batistoni, Evaluation of sorption and desorption characteristics of cadmium, lead and zinc on Amberlite IRC-718 iminodiacetic chelating ion exchanger, Talanta 57 (2002) 277–287.

[10] R.K. Sharma, N. Bhojak, S. Mittal, B.S. Garg, Chelating resins and their applications in the analysis of trace metal ions, Microchem. J. 61 (1999) 94–114.

[11] J. Lehto, A. Paajanen, R. Harjula, H. Leinonen, Hydrolysis and H^+/Na^+ exchange by Chelex 100 chelating resin, React. Polym. 23 (1994) 135–140.

[12] L.C. Lin, R.S. Juang, Ion-exchange equilibria of Cu(II) and Zn(II) from aqueous solutions with Chelex 100 and Amberlite IRC 748 resins, Chem. Eng. J. 112 (2005) 211–218.

[13] M.G. Rao, A.K. Gupta, E.S. Williams, A.A. Aguwa, Sorption of heavy metal ions on Chelex 100 resin, AIChE Symp. Ser. 78 (219) (1982) 103–111.

[14] C.N. Haas, V. Tare, Application of ion exchangers to recovery of metals from semiconductor wastes, React. Polym. 2 (1984) 61–70.

[15] V. Tare, S.B. Karra, C.N. Haas, Kinetics of metal removal by chelating resin from a complex synthetic wastewater, Water, Air, Soil Pollut. 22 (1984) 429–439.

[16] E. Korngold, N. Belayev, L. Aronov, S. Titelman, Influence of complexing agents on removal of metals from water by a cation exchanger, Desalination 133 (2001) 83–88.

[17] T.H. Karppinen, A.Y. Pentti, Evaluation of selective ion exchange for nickel and cadmium uptake from the rinse water of a plating shop, Sep. Sci. Technol. 35 (2000) 1619–1633.

[18] F. Gode, E. Pehlivan, A comparative study of two chelating exchange resins for the removal of chromium(III) from aqueous solution, J. Hazard. Mater. B100 (2003) 231–243.

[19] F. Mijangos, M. Diaz, Metal-proton equilibrium relations in a chelating iminodiacetic resin, Ind. Chem. Eng. Res. 31 (1992) 2524–2532.

[20] A.A. Zagorodni, D.N. Muiraviev, M. Muhammed, Separation of Zn and Cu using chelating ion exchangers and temperature variations, Sep. Sci. Technol. 32 (1997) 413–429.

[21] F. Helfferich, Ion Exchange, McGraw-Hill, New York, USA, 1962.

[22] S.H. Lin, C.D. Kiang, Chromic acid recovery from waste acid solution by an ion exchange process: equilibrium and column ion exchange modeling, Chemosphere 57 (2004) 789–793.

[23] A. Fermindez, M. Diaz, A. Rodrigues, Kinetic mechanisms in ion exchange processes, Chem. Eng. J. 57 (1995) 17–25.

[24] J.W. Coetzee, An activity model for multi-component ion exchange, Miner. Eng. 16 (2003) 519–522.

[25] H.S. Fogler, Elements of Chemical Reaction Engineering, second ed., Prentice Hall Inc., Englewood Cliffs, New Jersey, 1992, pp. 582–587.

[26] B. van Raij, J.O. Agbenin, Rate processes of calcium, magnesium and potassium desorption from variable-charge soils by mixed ion-exchange resins, Geoderma 93 (1999) 141–157.

[27] E. Hogfeldt, Comparison of some isotherms for representing ion-exchange equilibria, React. Polym. 23 (1994) 19–22.

[28] N.Z. Misak, Adsorption isotherms in ion exchange reactions. Further treatments and remarks on the application of the Langmuir isotherm, Colloids Surfaces A, Physicochem. Eng. Asp. 97 (1995) 129–140.

[29] R. Shah, S. Devi, Chelating resin containing s-bonded dithizone for separation of copper(II), nickel(II) and zinc(II), Talanta 45 (1998) 1089–1096.