Nickel(II) and zinc(II) removal using Amberlite IR-120 resin: Ion exchange equilibrium and kinetics

Pietro Escobar Franco [a], Márcia Teresinha Veit [a,*], Carlos Eduardo Borba [a], Gilberto da Cunha Gonçalves [b], Márcia Regina Fagundes-Klen [a], Rosangela Bergamasco [c], Edson Antonio da Silva [a], Pedro Yahico Ramos Suzaki [a]

[a] Western Paraná State University, Department of Chemical Engineering, Campus of Toledo, Rua da Faculdade, 645, Jardim La Salle, CEP 85903-000 Toledo, PR, Brazil
[b] Federal Technology University of Paraná, Campus of Toledo, Rua Cristo Rei, 19, Vila Becker, CEP 85902-490 Toledo, PR, Brazil
[c] State University of Maringá, Department of Chemical Engineering, Avenida Colombo, 5790, Bloco E-46, Sala 09, CEP 87020-900 Maringá, PR, Brazil

HIGHLIGHTS

▶ Amberlite IR 120 resin was used for the removal of zinc and nickel ions.
▶ The model used to describe equilibrium data was the mass action law.
▶ The non-ideal model was used to predict the equilibrium of the ternary system.
▶ The intraparticle diffusion described the ion exchange kinetics of binary systems.

ARTICLE INFO

ABSTRACT

In the present work, experimental data was obtained on ion exchange equilibrium for the binary systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+ and the ternary system $Ni^{2+}/Zn^{2+}/Na^+$, as well as on the kinetics of ion exchange for the binary systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+, using Amberlite IR 120 resin in closed batch system at 25 °C and starting pH of 4.5. The model used to describe equilibrium data was the law of mass action, considering both ideal and non-ideal behaviors to represent the experimental data. Bromley's and Wilson's models were used to describe non-ideality in the liquid phase and in the resin, respectively. The thermodynamic equilibrium constant and Wilson's parameters were obtained by fitting the model to experimental equilibrium data of each binary system. The non-ideal law of mass action best described the equilibrium for the binary systems. Based on these results, only the non-ideal law of mass action was used to predict the equilibrium for the ternary system, with the parameters of the binary systems being used. There was good agreement between the predicted and experimental values of the resin phase composition. Two models were used to describe the experimental data on ion exchange kinetics. The first one considered that ion exchange reaction was the limiting step of the overall mass transfer process, while the second one considered intraparticle diffusion as the limiting step. The latter was found to best describe the experimental data on ion exchange kinetics for binary systems.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Industrial activity has contributed notably to water contamination by various heavy metals. When released into the environment, these toxic, non-biodegradable metals can be hazardous to aquatic life and human health, for they can move up the food chain, accumulating along the way. Therefore, the removal of these pollutants is necessary, making it an object of constant scientific study.

For the removal of heavy metals from industrial effluents, literature presents processes such as chemical precipitation, electroflocculation, reverse osmosis, adsorption [1,2], and ion exchange [3–6]. Ion exchange processes using natural substances or synthetic resins exhibit satisfactory results for the removal of low concentrations of different heavy metals from effluents [5]. In these cases, chemical precipitation cannot achieve the required concentration for effluent discharge. Moreover, the resins can be easily regenerated and reused [7].

* Corresponding author. Tel.: +55 45 3379 7091; fax: +55 45 3379 7000.
  E-mail addresses: Pietro.Franco@ecocataratas.com.br (P.E. Franco), marcia_veit@yahoo.com.br (M.T. Veit), borba_deq@yahoo.com.br (C.E. Borba), cunha@utfpr.edu.br (Gilberto da Cunha Gonçalves), fagundes.klen@gmail.com (M.R. Fagundes-Klen), rosangela@deq.uem.br (R. Bergamasco), edsondeq@hotmail.com (E.A. da Silva), pedrosuzaki@hotmail.com (P.Y.R. Suzaki).

The design and efficient operation of an ion exchange process require equilibrium data for use in kinetic and mass transfer models, making the obtainment of equilibrium data a primary step for the development of the ion exchange process [8]. The isotherms fitted in the ion exchange process should be derived from the law of mass action (LMA), for this model takes into account the stoichiometry, the non-ideality of liquid and solid phases, and the ion–solid and ion–ion interactions. Many researchers [9,4,5,10–12], however, evaluated ion exchange equilibrium based on adsorption isotherm models.

Other studies show the use of the law of mass action to describe ion exchange equilibrium. Valverde et al. [13] obtained equilibrium data for the binary systems Cu^{2+}/Na^+, Cd^{2+}/Na^+, and Zn^{2+}/Na^+ using Amberlite IR-120 resin as ion exchanger. The activity coefficients for the solution and for the resin were calculated using Pitzer's and Wilson's models, respectively.

Equilibrium data was obtained by LIN and JUANG [14] for the binary systems Cu^{2+}/Na^+ and Zn^{2+}/Na^+ using Chelex 100 and Amberlite IRC 748 resins as ion exchangers. The authors used adsorption (Langmuir model) and ion exchange (LMA) isotherms to represent equilibrium data. The activity coefficient for the solution was calculated according to Debye-Huckel, Davies, and Pitzer models.

Borba et al. [6] used the law of mass action to predict ion exchange equilibrium for the ternary system $Ni^{2+}/Zn^{2+}/Na^+$ based on the binary systems Cu^{2+}/Na^+ and Zn^{2+}/Na^+. Bromley's and Wilson's models were used to calculate the activity coefficient for the solution and for the Amberlite IR-120 resin, respectively. Valverde et al. [15] and Petrus and Warchol [16] also used the law of mass action for Amberlite IR-120 resin and for clinoptilolite, respectively.

Determination of ion exchange kinetic parameters involves mathematical modeling and simulation. Alguacil et al. [17] obtained kinetic data for the binary system Cu^{2+}/H^+ using Amberlite IR-120 resin. The results pointed film diffusion as the limiting step of the process.

LIN and JUANG [18] used three models to represent ion exchange kinetic data for the binary systems Zn^{2+}/Na^+ and Cu^{2+}/Na^+ using Chelex-100 and Amberlite IRC 748 resins. Diffusion in the resin was assumed as the limiting step of the process both for the unreacted-core model and for the second model, which was described by Fick's first law. The ion exchange reaction was assumed as the limiting step of the process in the third model.

In this context, the present study was performed under experimental conditions that were similar to those from the galvanic industry effluents and evaluated different metallic ions which could be compared with results from the literature. This study aimed at investigating the kinetics of ion exchange for the binary systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+ and, based on the non-ideal law of mass action, predicting the ion exchange equilibrium for the ternary system $Ni^{2+}/Zn^{2+}/Na^+$ from the results obtained with the binary systems, employing Amberlite IR-120 in the Na^+ form.

2. Materials and methods

2.1. Chemicals

High purity (>99%) chemicals were employed. Solutions were prepared with distilled/deionized water. The following chemicals were employed: nickel(II) chloride ($NiCl_2.6H_2O$); zinc(II) chloride ($ZnCl_2$); sodium chloride; hydrochloric acid; sodium hydroxide, and hexane.

2.2. Ion exchanger

Amberlite IR-120 resin was used as the ion exchanger. Some properties of this resin are presented in Table 1. The resin was

washed with HCl (1 M), NaOH (1 M), and hexane in order to remove organic and inorganic impurities [19]. The column technique was then used to convert the resin to the Na^+ form. The resin was packed in a glass column with inner diameter of 0.9 cm and height of 30 cm. An ionic aqueous solution (6% NaCl, pH 6.5–6.8, prepared with distilled/deionized water) was fed to the bottom of the column by means of a peristaltic pump (Cole Parmer) at a constant flow rate (6 mL min^{-1}). The process was carried out until the equilibrium condition was met (effluent sodium concentration = feed sodium concentration). Distilled/deionized water was then fed to the column to remove excess sodium. The resin was subsequently oven-dried at 105 °C and stored in a desiccator.

2.3. Speciation diagram

To determine the ionic forms of nickel, zinc, and sodium in solution, speciation diagrams were simulated using the *software* HYDRA (*Hydrochemical Equilibrium-Constant Database*) [20]. Diagrams were simulated for the systems $NiCl_2/NaCl/H_2O$, $ZnCl_2/NaCl/H_2O$, and $NiCl_2/ZnCl_2/NaCl/H_2O$ considering a concentration of 10 meq L^{-1} (approximately 5 mM), which corresponds to the maximum concentration of each species in solution.

2.4. Ion exchange kinetics

Experimental data on ion exchange kinetics for the binary systems (Ni^{2+}/Na^+, Zn^{2+}/Na^+) was obtained in a closed batch system with total initial concentrations of 0.5 and 7.0 meq L^{-1}. The equipment was a refrigerated orbital shaking incubator (Tecnal TE-424). Tests were performed at constant temperature (25 ± 0.1 °C). 0.1 L aliquots of an ionic solution with known composition and pH 4.5 (adjusted with HCl 1 M) were added to Erlenmeyer flasks containing different amounts of resin in the Na^+ form. The accuracy in weighing the masses of resin was 0.0001 g. The suspension was kept under agitation (150 rpm). Samples were taken at predetermined time intervals and the contents of the flasks, filtered (45 μm Millipore membrane). The concentrations of nickel and zinc in the filtrate were determined by atomic absorption spectrophotometry (Varian SpectrAA-10 Plus) and that of sodium by flame photometry (DIGIMED DM-61). The pH of the samples was also measured (DIGIMED DM-22). All experiments were carried out in duplicate.

The heavy metal concentration (Ni^{2+} or Zn^{2+}) in the resin was obtained from a mass balance, represented in Eq. (1). The concentration of Na^+ in the resin was then obtained from Eq. (2).

$$q_j(t) = \frac{(C_j^0 - C_j(t))V}{m} \tag{1}$$

$$q_{Na}(t) = CEC - q_j(t) \tag{2}$$

In these equations, $q_j(t)$ and $q_{Na}(t)$ are the concentrations of species j (Ni^{2+} or Zn^{2+}) and sodium in the resin at time t (meq g^{-1}), $C_j^0(t)$ is the initial concentration of species j in the solution (meq L^{-1}), $C_j(t)$ is the concentration of species j in the solution at

Table 1
Characteristics of Amberlite IR-120 resin. *Source*: Alguacil et al. [17], with modifications.

Characteristic	Cationic resin
Active group	Sulfonic (R-SO$_3^-$)
Matrix	Polystyrene–divinylbenzene copolymer
Ionic form	Na^+
Average particle size (mm)	0.5 (spherical particles)
Working pH range	0–14
Cation Exchange Capacity (*CEC*)	5 meq g^{-1} (dry basis)
Maximum operating temperature	120 °C
Manufacturer	Rhom & Haas

time t (meq L^{-1}), m is the mass of resin (dry basis) (g), V is the volume of solution (L) and CEC is the total cation exchange capacity of the resin (meq g^{-1}). The value of the CEC for Amberlite IR-120 in the sodium form was determined by Borba et al. [6] as 5.13 meq g^{-1}.

The ionic fractions of the species in solution and in the resin were determined from Eqs. (3) and (4), respectively, where $x_j(t)$ is the ionic fraction of species j in the solution at time t, $y_j(t)$ is the ionic fraction of species j in the resin at time t, and C_0 is the total initial concentration of the solution (meq L^{-1}).

$$x_j(t) = \frac{C_j(t)}{C_0} \tag{3}$$

$$y_j(t) = \frac{q_j(t)}{CEC} \tag{4}$$

2.5. Ion exchange equilibrium

Experimental ion exchange equilibrium data for the binary systems (Ni^{2+}/Na^+ and Zn^{2+}/Na^+) and for the ternary system ($Ni^{2+}/Zn^{2+}/Na^+$) was obtained in a closed batch system with total concentrations of 5 and 10 meq L^{-1} following the methods presented in Section 2.4. All experiments were conducted under the same conditions of temperature, agitation, initial pH, and initial volume of solution. After the equilibrium time (determined by the kinetic experiments), samples were withdrawn and filtered (45 µm Millipore membrane). The pH of the samples and the concentration of nickel, zinc, and sodium in the filtrate were determined. All experiments were carried out in duplicate.

The heavy metal concentration (Ni^{2+} or Zn^{2+}) in the resin at equilibrium was obtained from a mass balance, represented in Eq. (5). The concentration of Na^+ in the resin at equilibrium was then obtained from Eq. (6).

$$q_j^* = \frac{(C_j^0 - C_j^*)V}{m} \tag{5}$$

$$q_{Na}^* = CEC - q_j^* \tag{6}$$

In these equations, C_j^* is the concentration of species j in the solution at equilibrium (meq L^{-1}) and q_j^* and q_{Na}^* are the concentrations of species j and sodium, respectively, in the resin at equilibrium (meq g^{-1}).

The ionic fractions of the species, both in solution and in the resin, at equilibrium were determined from Eqs. (7) and (8), respectively, where x_j^* is the ionic fraction of species j in solution at equilibrium, y_j^* is the ionic fraction of species j in the resin at equilibrium, and C_T is the total concentration of the solution (meq L^{-1}).

$$x_j^* = \frac{C_j^*}{C_T} \tag{7}$$

$$y_j^* = \frac{q_j^*}{CEC} \tag{8}$$

3. Mathematical modeling

3.1. Modeling ion exchange equilibria – binary system

Ion exchange between cations A^{z_A} and B^{z_B} can be represented by the reversible stoichiometric reaction presented as Eq. (9), where z_j is the charge of species j and subscripts R and S represent resin and solution, respectively.

$$z_B A_S^{z_A} + z_A B_R^{z_B} \leftrightarrow z_B A_R^{z_A} + z_A B_S^{z_B} \tag{9}$$

The thermodynamic equilibrium constant (K_{AB}) for ion exchange between species A and B is defined by Eq. (10), where C_j^* is the ionic concentration of species j in solution at equilibrium,

y_j^* is the ionic fraction of species j in the resin at equilibrium, γ_{Sj} is the activity coefficient of species j in solution, and γ_{Rj} is the activity coefficient of species j in the resin.

$$K_{AB} = \left(\frac{y_A^* \gamma_{R_A}}{C_A^* \gamma_{S_A}}\right)^{z_B} \left(\frac{C_B^* \gamma_{S_B}}{y_B^* \gamma_{R_B}}\right)^{z_A} \tag{10}$$

Considering ideal behavior in both phases, the activity coefficients are equal to 1, and Eq. (10) becomes Eq. (11).

$$K_{AB} = \left(\frac{y_A^*}{C_A^*}\right)^{z_B} \left(\frac{C_B^*}{y_B^*}\right)^{z_A} \tag{11}$$

When non-ideal behavior is considered, it is necessary to determine the activity coefficient for both phases. Bromley's model [21], given by Eq. (12), was used to calculate the activity coefficient of species j in solution.

$$\ln \gamma_{S_j} = \frac{-A z_j^2 \sqrt{I}}{1 + \sqrt{I}} + F_j \tag{12}$$

The ionic strength (I) was calculated using Eq. (13), where n is the number of species in solution and m_j is the molality of species j in the solution. The term F_j is the sum of the interaction parameters. For each species j in a multicomponent solution, this term is given by Eq. (14).

$$I = \frac{1}{2} \sum_{j=1}^{n} z_j^2 m_j \tag{13}$$

$$F_j = \sum_i \dot{B}_{ji} Z_{ji}^2 m_i \tag{14}$$

where

$$Z_{ji} = \frac{z_i + z_j}{2} \tag{15}$$

$$\dot{B}_{ji} = \frac{(0.06 + 0.6 B_{ji})|z_i z_j|}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} + B_{ji} \tag{16}$$

Subscripts i and j refer to anions and cations in solution, respectively. Parameters A and B_{ji} are temperature dependent. Zemaitis et al. [22] reported values for these parameters.

Wilson's model [23], given by Eq. (17), where Λ are its interaction parameters, was used to determine the activity coefficient of species i in the resin.

$$\ln \gamma_{R_i} = 1 - \ln \left(\sum_{j=1}^{n} y_j^* \Lambda_{ij}\right) - \sum_{k=1}^{n} \left[\frac{y_k^* \Lambda_{ki}}{\sum_{j=1}^{L} y_j^* \Lambda_{kj}}\right] \tag{17}$$

3.1.1. Method of parameters identification

The modeling of experimental data on ion exchange equilibrium for binary systems using Eq. (10) requires knowledge of the interaction parameters of Wilson's model and of the thermodynamic equilibrium constant. In contrast, modeling from Eq. (11) only requires that the thermodynamic equilibrium constant is known.

In the present work, the model parameters (K_{AB}, Λ_{AB}, Λ_{BA}) were estimated with the nonlinear identification procedure using the experimental data and the least squares statistical method to form the objective function. The parameter values were obtained by minimizing the objective function (Eq. (18)), where M is the number of equilibrium data points and N, the number of cationic species.

$$F_{OBJ} = \sum_{i=1}^{N} \left[\sum_{j=1}^{M} (y_{ji}^{exp} - y_{ji}^{mod})^2\right] \tag{18}$$

The optimization method of Nelder and Mead [24], coded in Fortran, was used. The procedure was carried out for the binary

systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+. The Newton method, written in Fortran, was used to solve equilibrium models.

3.2. Modeling ion exchange equilibria – ternary system

The ion exchange reactions occurring in the ternary system $Ni^{2+}/Zn^{2+}/Na^+$ can be represented by the following stoichiometric equations:

$$Ni_S^{2+} + 2Na_R^+ \leftrightarrow Ni_R^{2+} + 2Na_S^+ \tag{19}$$

$$Zn_S^{2+} + 2Na_R^+ \leftrightarrow Zn_R^{2+} + 2Na_S^+ \tag{20}$$

$$Ni_S^{2+} + Zn_R^+ \leftrightarrow Ni_R^{2+} + Zn_S^+ \tag{21}$$

The thermodynamic equilibrium constants are given by:

$$K_{NiNa} = \left(\frac{\gamma_{S_{Na}} C_{Na}^*}{\gamma_{R_{Na}} y_{Na}}\right)^2 \left(\frac{\gamma_{R_{Ni}} y_{Ni}}{\gamma_{S_{Ni}} C_{Ni}^*}\right) \tag{22}$$

$$K_{ZnNa} = \left(\frac{\gamma_{S_{Na}} C_{Na}^*}{\gamma_{R_{Na}} y_{Na}}\right)^2 \left(\frac{\gamma_{R_{Zn}} y_{Zn}}{\gamma_{S_{Zn}} C_{Zn}^*}\right) \tag{23}$$

$$K_{ZnNi} = \left(\frac{\gamma_{S_{Ni}} C_{Ni}^*}{\gamma_{R_{Ni}} y_{Ni}}\right) \left(\frac{\gamma_{R_{Zn}} y_{Zn}}{\gamma_{S_{Zn}} C_{Zn}^*}\right) \tag{24}$$

In addition to the equations that define the equilibrium constant, it is necessary to consider the constraint involving the ionic fraction for the resin, given by the following equation:

$$y_{Ni} + y_{Zn} + y_{Na} = 1 \tag{25}$$

For a given solution composition $(C_{Ni}^*, C_{Zn}^*, C_{Na}^*)$, the respective ionic composition of the resin $(y_{Ni}^*, y_{Zn}^*, y_{Na}^*)$ in equilibrium with the solution can be determined if the equilibrium constants are known and the activity coefficients of both phases can be predicted [25]. The calculation of the resin composition from a solution composition can be performed by solving a nonlinear system, which may be composed of any three of the four Eqs. (22)–(25). In the present work, Eqs. 22, 23, and 25 were used.

The values of the thermodynamic equilibrium constants (K_{NiNa}, K_{ZnNa}) and Wilson's interaction parameters $(\Lambda_{NiNa}, \Lambda_{NaNi}, \Lambda_{ZnNa}, \Lambda_{NaZn})$ obtained for the binary systems Ni^{2+}/Na^+ and Zn^{+2}/Na^+ were used for the prediction of the ternary ion exchange equilibrium. Wilson's interaction parameters of the binary system Ni^{2+}/Zn^{2+} were obtained from the following equations [26]:

$$\Lambda_{NiNa}\Lambda_{NaZn}\Lambda_{ZnNi} = \Lambda_{NaNi}\Lambda_{ZnNa}\Lambda_{NiZn} \tag{26}$$

$$\Lambda_{ZnNi}\Lambda_{NiZn} = 1 \tag{27}$$

3.3. Modeling ion exchange kinetics

To describe the ion exchange kinetics for the binary systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+, two models were used. For the first one, the ion exchange reaction was considered to be the limiting step of the overall mass transfer process. For the second one, intrapar-
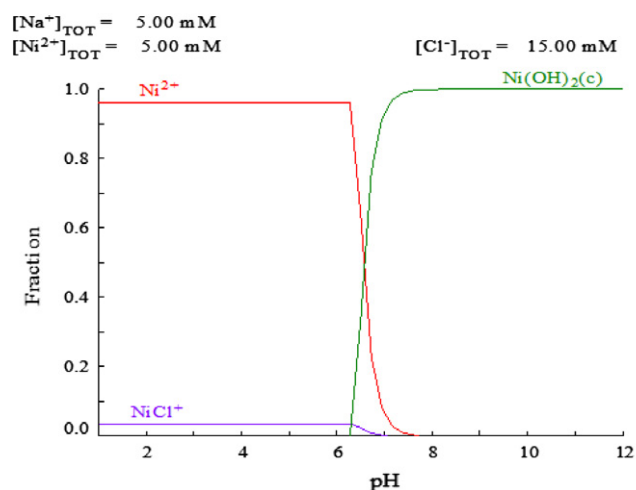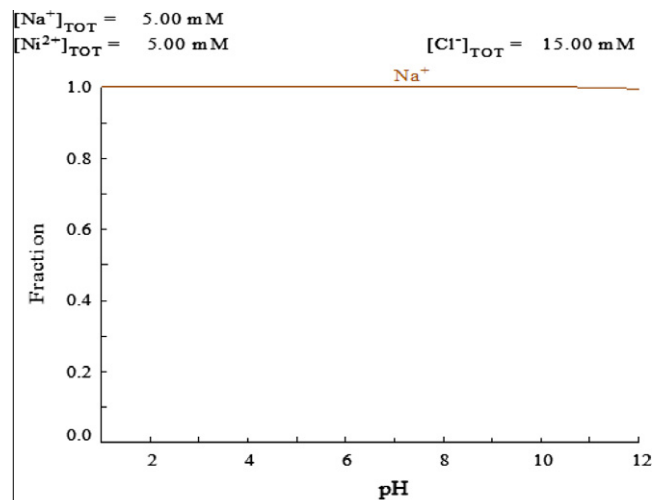

Fig. 1. Speciation in the system $NiCl_2/NaCl/H_2O$ as a function of pH. (c) = complex.

ticle diffusion was considered to be the limiting step. Both models are composed of equations that describe the mass transfer rate and the mass balance equations.

3.3.1. Limiting step: ion exchange reaction

In this model the resistance to mass transfer in the outer film and inside the particle was considered negligible. Thus, the kinetics of ion exchange between species A and B is described by Eqs. (28) and (29), where k_D and k_R are respectively the direct and reverse kinetic constants of the ion exchange reaction.

$$\frac{dy_A(t)}{dt} = k_D (C_A(t)\gamma_{S_A})^{z_B}(y_B(t)\gamma_{R_B})^{z_A} - k_R(y_A(t)\gamma_{R_A})^{z_B}(C_B(t)\gamma_{S_B})^{z_A} \tag{28}$$

$$\frac{dy_B(t)}{dt} = -\frac{dy_A(t)}{dt} \tag{29}$$

Table 2
pH values obtained during ion exchange kinetics and equilibrium experiments.

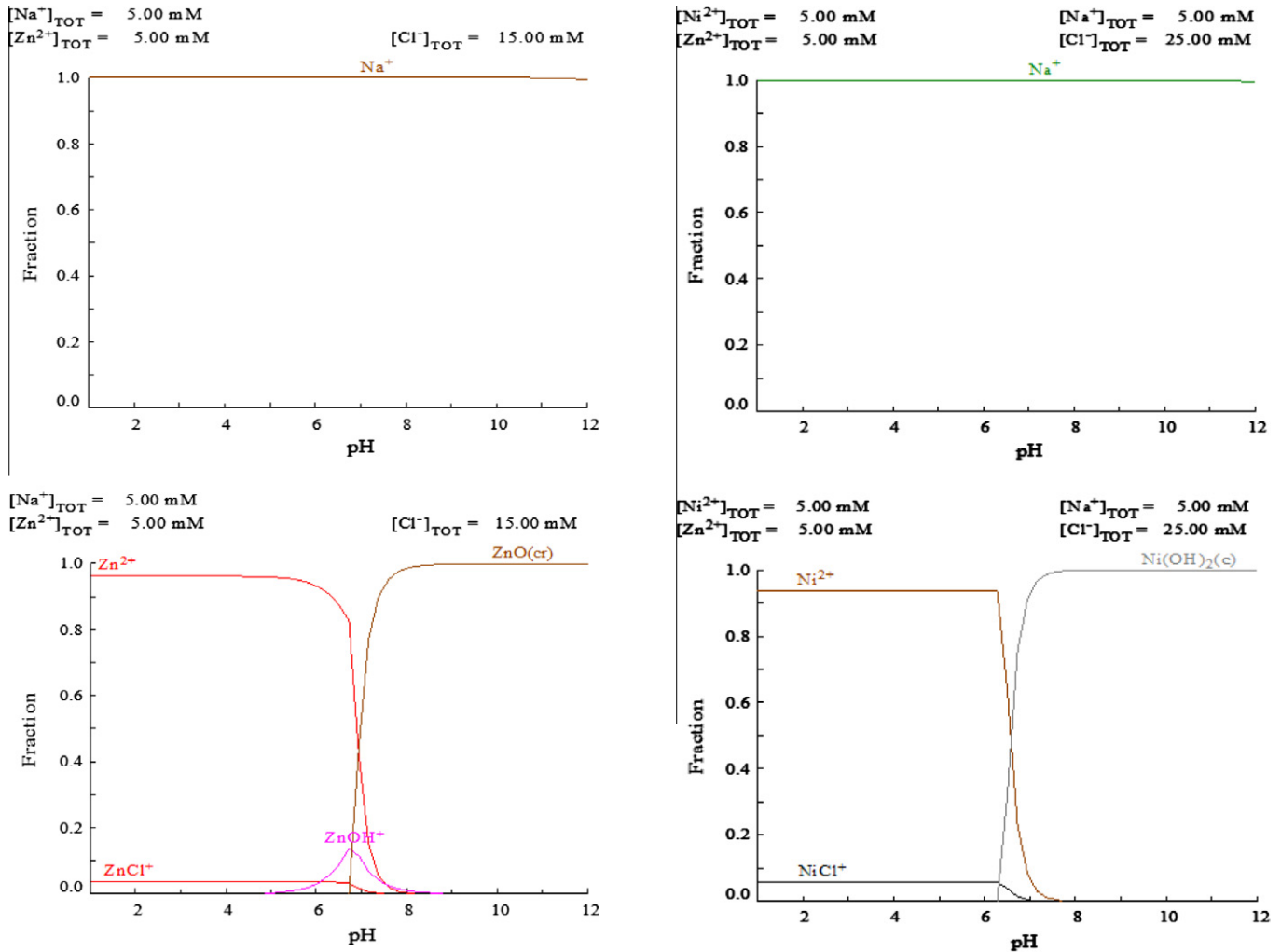| System	Ni^{2+}/Na^+ 0.5 meq L^{-1}	Ni^{2+}/Na^+ 7.0 meq L^{-1}	Zn^{2+}/Na^+ 0.5 meq L^{-1}	Zn^{2+}/Na^+ 7.0 meq L^{-1}		
pH values – ion exchange kinetics						
Minimum	4.5	4.5	4.5	4.5		
Maximum	4.8	5.4	4.7	5.3		
System	Ni^{2+}/Na^+ 5 meq L^{-1}	Ni^{2+}/Na^+ 10 meq L^{-1}	Zn^{2+}/Na^+ 5 meq L^{-1}	Zn^{2+}/Na^+ 10 meq L^{-1}	$Ni^{2+}/Zn^{2+}/Na^+$ 5 meq L^{-1}	$Ni^{2+}/Zn^{2+}/Na^+$ 10 meq L^{-1}
pH values – ion exchange equilibrium						
Minimum	4.5	4.5	4.5	4.5	4.5	4.5
Maximum	5.6	5.9	5.5	5.8	5.9	6.2

Fig. 2. Speciation in the system ZnCl₂/NaCl/H₂O as a function of pH. (cr) = crystal.

The mass balance in a closed system for components A and B (A = Ni²⁺ or Zn²⁺; B = Na⁺) is given by Eqs. (30) and (31), and the applied initial conditions are described by Eqs. (32)–(35).

$$y_A(t) = \frac{1}{CEC}\frac{V}{m}(C_A^0 - C_A(t)) \tag{30}$$

$$y_A(t) + y_B(t) = 1 \tag{31}$$

$$C_A(0) = C_A^0 \tag{32}$$

$$C_B(0) = 0 \tag{33}$$

$$y_A(0) = 0 \tag{34}$$

$$y_B(0) = CEC \tag{35}$$

3.3.2. Limiting step: intraparticle diffusion

Instantaneous equilibrium at the solution/resin interface and negligible resistance to mass transfer in the outer film were assumed in this model. This way, the ion exchange kinetics between species A and B is described by Eqs. (36) and (37), where K_{S_A} is the volumetric coefficient of intraparticle mass transfer and y_A^* is the ionic fraction of species A in the resin in equilibrium with species A in solution.

$$\frac{dy_A(t)}{dt} = K_{S_A}(y_A^*(t) - y_A(t)) \tag{36}$$
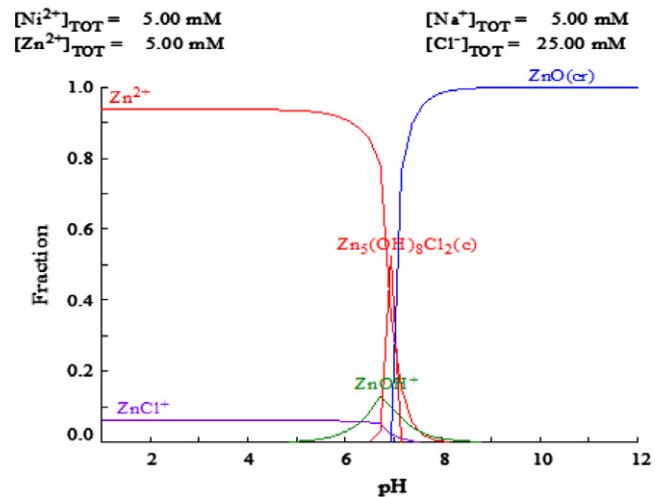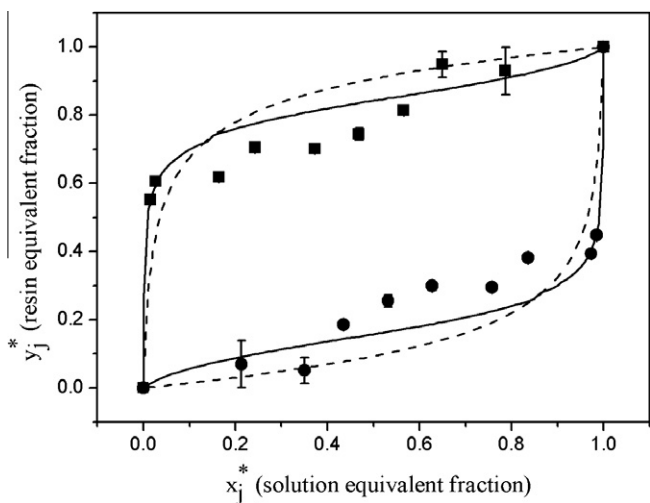
$$\frac{dy_B(t)}{dt} = -\frac{dy_A(t)}{dt} \tag{37}$$

Fig. 3. Speciation in the system NiCl₂/ZnCl₂/NaCl/H₂O as a function of pH. (c) = complex, (cr) = crystal.

Eq. (36), called Linear Driving Force (LDF) model, is an approximation of Fick's second law that was originally proposed by Glueckauf and Coates [27]. The volumetric coefficient of intraparticle mass transfer can be related to the intraparticle diffusion coefficient by Eq. (38) [27], where r_p is the particle radius of the ion exchange resin.

Table 3
Fitted parameters of the law of mass action (LMA), objective function, and coefficients of determination – binary systems.

System	Non-ideal LMA	Ideal LMA
Ni^{2+}/Na^+	$K_{NiNa} = 1.59$	
	$\Lambda_{NiNa} = 3.69$	$K_{NiNa} = 0.29$
	$\Lambda_{NaNi} = 1.17$	$F_{obj} = 0.37$
	$F_{obj} = 0.03$	$r^2 = 0.75$
	$r^2 = 0.97$	
Zn^{2+}/Na^+	$K_{ZnNa} = 1.58$	
	$\Lambda_{ZnNa} = 1.73$	$K_{ZnNa} = 0.20$
	$\Lambda_{NaZn} = 4.01$	$F_{obj} = 0.20$
	$F_{obj} = 0.05$	$r^2 = 0.89$
	$r^2 = 0.93$	

Fig. 4. Isotherm for the system Ni^{2+}/Na^+ (C_T = 5 meq L^{-1}, T = 298 K, $pH_{initial}$ = 4.5). ■ Experimental Ni^{2+}, ● Experimental Na^+, — Non-ideal law of mass action, - - - - Ideal law of mass action.
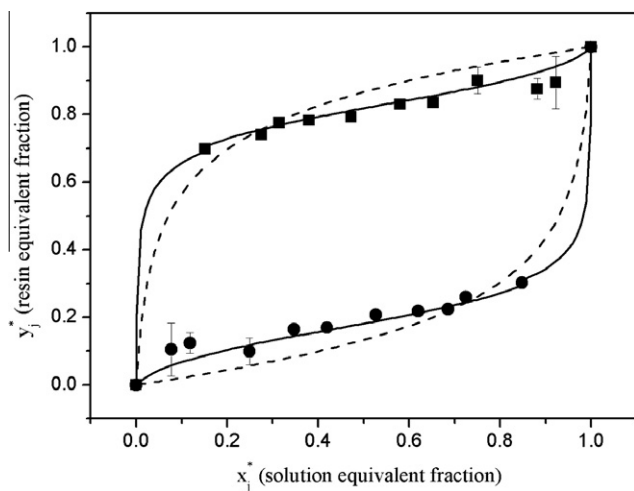
Fig. 5. Isotherm for the system Ni^{2+}/Na^+ (C_T = 10 meq L^{-1}, T = 298 K, $pH_{initial}$ = 4.5). ■ Experimental Ni^{2+}, ● Experimental Na^+, — Non-ideal law of mass action, - - - - Ideal law of mass action.

The mass balance in a closed system for components A and B is given by Eqs. (30) and (31), and the initial conditions are described by Eqs. (32)–(35). The ionic fraction in the resin at equilibrium was calculated by Eq. (10), assuming $C_A^* = C_A$, for the diffusion resistance in the outer film was neglected.

$$K_{S_j} = 1 \times \frac{D}{l}$$ (8)
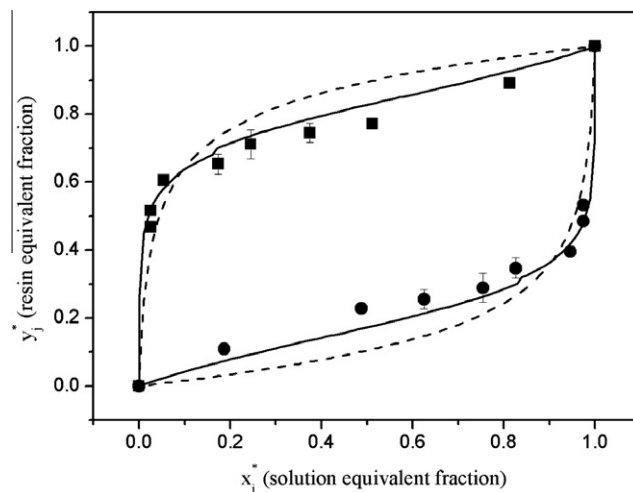
Fig. 6. Isotherm for the system Zn^{2+}/Na^+ (C_T = 5 meq L^{-1}, T = 298 K, $pH_{initial}$ = 4.5). ■ Experimental Zn^{2+}, ● Experimental Na^+, — Non-ideal law of mass action, - - - - Ideal law of mass action.
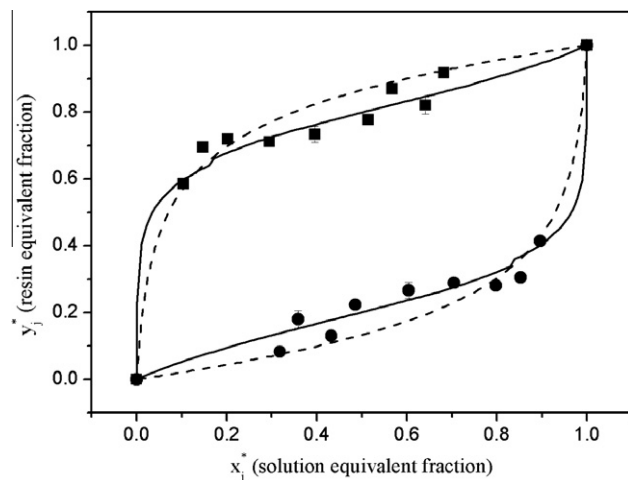

Fig. 7. Isotherm for the system Zn^{2+}/Na^+ (C_T = 10 meq L^{-1}, T = 298 K, $pH_{initial}$ = 4.5). ■ Experimental Zn^{2+}, ● Experimental Na^+, — Non-ideal law of mass action, - - - - Ideal law of mass action.

3.3.3. Methods of solution and parameters identification

The modeling of experimental data on ion exchange kinetics for binary systems using the models presented in Sections 3.3.1 and 3.3.2 requires the values of k_D and K_{Sj}. In the present work, these model parameters were estimated via nonlinear identification procedure using the experimental data and the least squares statistical method to form the objective function. The parameter values were obtained by minimizing the objective function given by Eq. (18) through the optimization method of NELDER and MEAD [24], written in Fortran. The procedure was carried out for the binary systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+. The Gear method, coded in Fortran, was used to solve kinetic models.
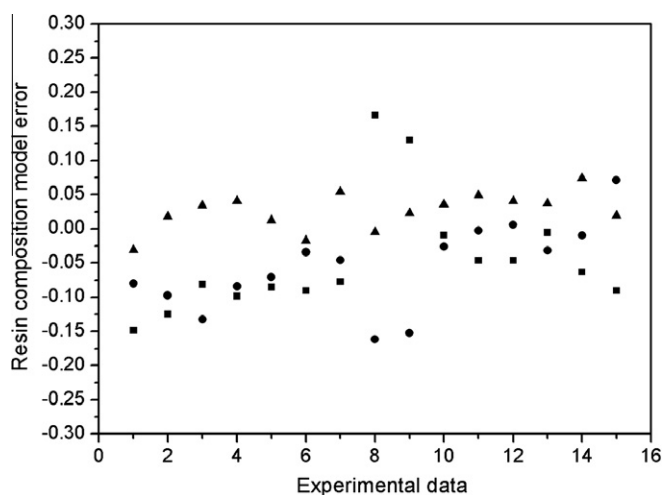
4. Results and discussion

4.1. pH results and speciation diagram

Some pH values do not allow the complete speciation of the ions of interest or can promote the precipitation of compounds [9]. The fraction of free ions in solution is, therefore, strongly dependent on pH and concentration of the elements in the medium.

Table 4
Predicted and experimentally determined equilibrium resin composition for the ternary system.

Experimental solution equivalent fraction			Experimental resin equivalent fraction			Predicted resin equivalent fraction		
x^*_{Ni}	x^*_{Zn}	x^*_{Na}	y^*_{Ni}	y^*_{Zn}	y^*_{Na}	y^*_{Ni}	y^*_{Zn}	y^*_{Na}
5 meq L^{-1}								
0.0837	0.0646	0.8517	0.5001	0.1169	0.3829	0.3268	0.3634	0.3098
0.4412	0.1563	0.4025	0.7068	0.1473	0.1458	0.5511	0.2994	0.1494
0.0108	0.0177	0.9715	0.2746	0.2368	0.4886	0.1542	0.3833	0.4625
0.0671	0.0397	0.8931	0.3249	0.2991	0.3760	0.3479	0.3166	0.3355
0.1857	0.1115	0.7029	0.3492	0.3601	0.2907	0.4090	0.3524	0.2386
0.3387	0.2430	0.4183	0.3706	0.4351	0.1942	0.4307	0.4169	0.1525
0.0341	0.0679	0.8980	0.1637	0.4467	0.3896	0.1803	0.4707	0.3490
0.1098	0.1957	0.6945	0.1622	0.5222	0.3155	0.2385	0.5218	0.2397
0.1966	0.3871	0.4164	0.1531	0.6751	0.1719	0.2566	0.5916	0.1518
10 meq L^{-1}								
0.1318	0.1201	0.7482	0.1201	0.2980	0.3229	0.2814	0.3690	0.3496
0.2084	0.1829	0.6087	0.1829	0.3012	0.3120	0.3210	0.3889	0.2901
0.2449	0.2318	0.5233	0.2318	0.2922	0.2963	0.3271	0.4140	0.2589
0.3235	0.2621	0.4145	0.2621	0.3339	0.2617	0.3744	0.4069	0.2187
0.3534	0.2862	0.3605	0.2862	0.3564	0.2136	0.3856	0.4154	0.1990
0.3776	0.2946	0.3277	0.2946	0.3922	0.1713	0.3988	0.4146	0.1866
0.4262	0.3277	0.2462	0.3277	0.3927	0.2096	0.4192	0.4266	0.1542

Fig. 8. Error diagram for the ternary system (■ Ni^{2+}, ● Zn^{2+}, ▲ Na^{+}).

Table 5
Fitted parameters of the kinetic models and coefficients of determination.

System	C_0 (meq L^{-1})	Limiting step	
		Ion exchange reaction	Intraparticle diffusion
Ni^{2+}/Na^{+}	0.5	$k_D = 0.05$ $r^2 = 0.81$	$K_S = 0.004$ $r^2 = 0.99$
Ni^{2+}/Na^{+}	7	$k_D = 0.22$ $r^2 = 0.50$	$K_S = 0.042$ $r^2 = 0.97$
Zn^{2+}/Na^{+}	0.5	$k_D = 0.06$ $r^2 = 0.77$	$K_S = 0.003$ $r^2 = 0.98$
Zn^{2+}/Na^{+}	7	$k_D = 0.32$ $r^2 = 0.47$	$K_S = 0.033$ $r^2 = 0.95$

an error of less than 6%. Therefore, the uptake of H^{+} ions could be assumed as negligible.

4.2. Ion exchange equilibrium

Experimental data on ion exchange equilibrium was obtained for the binary systems Ni^{2+}/Na^{+} and Zn^{2+}/Na^{+} with total concentrations of 5 and 10 meq L^{-1}. The non-ideal (Eq. (10)) and ideal (Eq. (11)) law of mass action were used as models to describe the equilibrium of these systems. In the non-ideal case, Bromley's model [21] was used to calculate the activity coefficient of the species in liquid phase. The parameters of Bromley's model were: $A = 0.5162$, $B_{NiCl} = 0.1039$, $B_{ZnCl} = 0.0364$, and $B_{NaCl} = 0.0574$ [22]. These parameters are valid for ionic strength of less than 6 molal and temperature of 25 °C. In the present study, the maximum calculated value of the ionic strength was 0.011 molal, which corresponds to a total concentration of 10 meq L^{-1}. Wilson's model [23] was used to calculate the activity coefficient for the resin. The parameters obtained from a nonlinear fitting of the ideal and non-ideal models to experimental equilibrium data are presented in Table 3.

Valverde et al. [13] obtained experimental data on ion exchange equilibrium for the binary systems Cu^{2+}/Na^{+}, Zn^{2+}/Na^{+}, and Cd^{2+}/Na^{+} using Amberlite IR 120 resin in the concentration range 50–100 meq L^{-1}. These values are high, as the ion exchange process is preferably applied to diluted systems and, therefore, equilibrium data obtained for concentrated systems has little practical utility. Borba et al. [6] obtained experimental equilibrium data using Amberlite IR 120 resin for the systems Cu^{2+}/Na^{+}, Zn^{2+}/Na^{+}, and

The pH of the solution was adjusted to 4.5 at the beginning of each experiment, and measured at the end of each one, when equilibrium was reached in the system. Table 2 shows the highest and lowest pH values obtained for the experiments of ion exchange kinetics and equilibrium.

Figs. 1–3 present the speciation diagrams simulated for each system (binary and ternary) with concentration of 10 meq L^{-1} (5.0 mM for Ni^{2+}, Zn^{2+}, and Na^{+}). This concentration corresponds to the highest concentration of species in solution used in the ion exchange kinetics and equilibrium experiments.

Based on the speciation diagrams (Figs. 1 and 2) and measured pH variations (Table 2) for the binary systems (Ni^{2+}/Na^{+} and Zn^{2+}/Na^{+}), it can be observed that species Ni^{2+}, Zn^{2+}, and Na^{+} are predominant (approximately 100%) in the solution used in the experiments. Equilibrium experiments with the ternary system Ni^{2+}/Zn^{2+}/Na^{+} (Fig. 3, Table 2) are an exception, as the concentration of Zn^{2+} ions is between 90% and 95% for the measured pH range.

Based on the pH results and speciation diagrams, species H^{+}, Na^{+}, Ni^{2+}, and Zn^{2+} can participate in the ion exchange process. However, the electroneutrality of the solution for the binary and ternary systems, which was evaluated taking into account the presence of only Na^{+}, Ni^{2+}, and Zn^{2+} species, was maintained within

Fig. 9. Kinetics for the Ni^{2+}/Na^+ system. Limiting step: ion exchange reaction (a) or intraparticle diffusion (b). $C_0 = 0.5$ meq L^{-1}; $T = 298$ K; $pH_{initial} = 4.5$. ■ Experimental Ni^{2+}, ● Experimental Na^+, — Model Ni^{2+}, ---- Model Na^+.
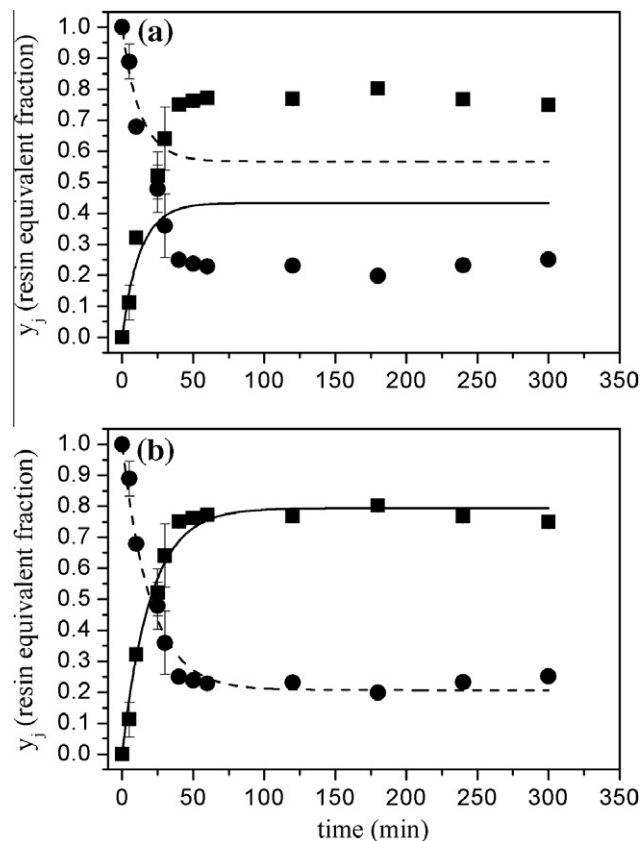

Fig. 10. Kinetics for the Ni^{2+}/Na^+ system. Limiting step: ion exchange reaction (a) or intraparticle diffusion (b). $C_0 = 7.0$ meq L^{-1}; $T = 298$ K; $pH_{initial} = 4.5$. ■ Experimental Ni^{2+}, ● Experimental Na^+, — Model Ni^{2+}, ---- Model Na^+.

Zn^{2+}/Cu^{2+} in the concentration range 1–5 meq L^{-1}, with $pH_{initial} = 4$ at 25 °C. The non-ideal law of mass action was used to describe equilibrium data. For the binary system Zn^{2+}/Na^+ the following values were obtained for the model parameters: $K_{ZnNa} = 0.38$, $\Lambda_{ZnNa} = 2.07$, and $\Lambda_{NaZn} = 1.05$. The values of these parameters differ from those presented in Table 3, probably due to the experimental conditions adopted in each study (concentration range and initial pH).

The experimental ion exchange isotherms and those simulated by the models (ideal and non-ideal law of mass action) are shown in Figs. 4–7 for each binary system and for each total concentration. In Figs. 4 and 5, which correspond to the system Ni^{2+}/Na^+, the shape of the curves indicates higher affinity of Ni^{2+} species with the resin. In Figs. 6 and 7, which correspond to the system Zn^{2+}/Na^+, the shape of the curves indicates higher affinity of Zn^{2+} species with the resin. Additionally, the values of the thermodynamic equilibrium constants (Table 3) for each system suggest the following order of affinity of Amberlite IR 120 resin with the studied species: $Ni^{2+} \approx Zn^{2+} > Na^+$.

The shape of the experimental isotherms was well described by both models. However, based on the values of the objective function and the coefficients of determination, shown in Table 3, the non-ideal law of mass action was found to best describe the experimental data, showing the non-ideal behavior of the investigated systems. According to Sandler [28], electrolytic systems exhibit deviation from ideality due to ion-ion and ion-solvent short-range electrostatic interactions (van der Waals force) and long-range interactions (coulombic force). At low concentrations, the average distance between ions is large and, therefore, only the long-range interactions remain important. At high concentrations, ions also interact through short-range forces. Consequently, even at low concentrations, these solutions have a strong non-ideal behavior and the activity coefficient can deviate significantly from one.

For the ternary system $Ni^{2+}/Zn^{2+}/Na^+$, experimental data on ion exchange equilibrium was obtained for the total concentrations of 5 and 10 meq L^{-1}. Considering the results observed for the binary systems, only the non-ideal law of mass action was used to describe the ion exchange equilibrium for the ternary system. In this procedure, the parameters obtained for the binary systems (thermodynamic equilibrium constant and Wilson's interaction parameters) were used. Wilson's interaction parameters Λ_{NiZn} and Λ_{ZnNi} were determined as 2.77 and 0.36 from Eqs. (26) and (27), respectively. Table 4 shows experimental equilibrium data and the values predicted by the model. Fig. 8 presents the error diagram for the resin composition estimation for the ternary system. The diagram indicates that the residue is between 0.17 and −0.15 for Ni^{2+}, between 0.07 and −0.17 for Zn^{2+}, and between 0.07 and −0.03 for Na^+. It is important to note that the distribution of residues was random. To assess the quality of prediction of the ion exchange equilibrium for the ternary system by the non-ideal law of mass action, coefficients of determination and variance were calculated. The average values for these parameters were 0.88 and 0.04, respectively.

4.3. Ion exchange kinetics

Experimental data on ion exchange kinetics was obtained for the binary systems Ni^{2+}/Na^+ and Zn^{2+}/Na^+ with initial concentrations of 0.5 and 7.0 meq L^{-1}. For both binary systems, equilibration time was approximately 600 min with initial concentration of 0.5 meq L^{-1} and 75 min with 7.0 meq L^{-1}. Two mathematical models were used to describe the kinetic data. For the first model, the

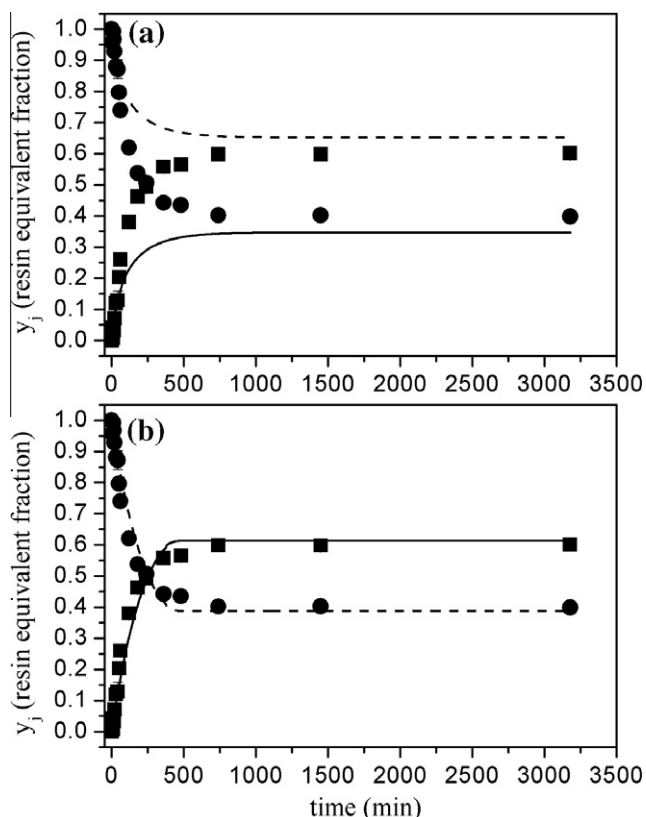**Fig. 11.** Kinetics for the Zn^{2+}/Na^+ system. Limiting step: ion exchange reaction (a) or intraparticle diffusion (b). $C_0 = 0.5$ meq L^{-1}; $T = 298$ K; $pH_{initial} = 4.5$. ■ Experimental Zn^{2+}, ● Experimental Na^+, — Model Zn^{2+}, ---- Model Na^+.
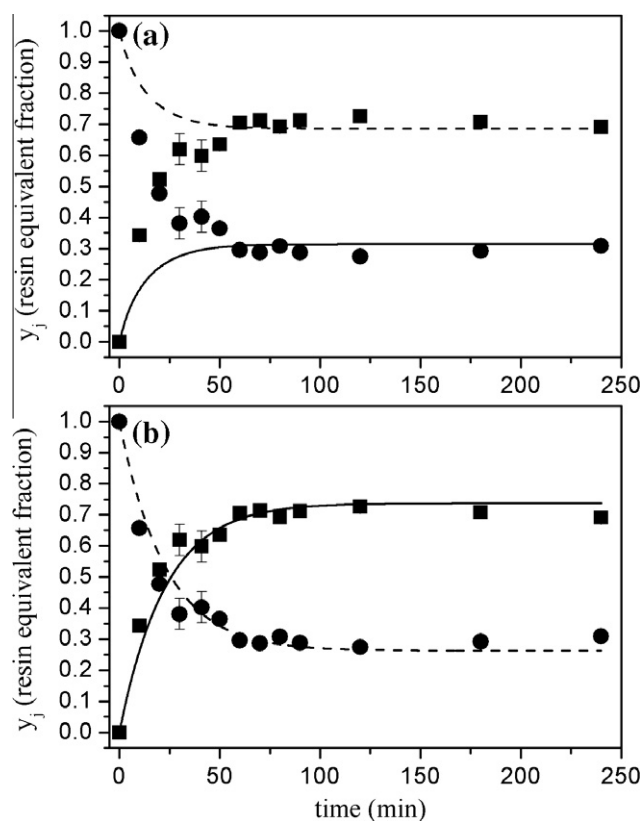

Fig. 12. Kinetics for the Zn^{2+}/Na^+ system. Limiting step: ion exchange reaction (a) or intraparticle diffusion (b). $C_0 = 7.0$ meq L^{-1}; $T = 298$ K; $pH_{initial} = 4.5$. ■ Experimental Zn^{2+}, ● Experimental Na^+, — Model Zn^{2+}, ---- Model Na^+.

ion exchange reaction was considered to be the limiting step of the overall mass transfer process. As for the second model, intraparticle diffusion was considered to be the limiting step. Table 5 lists the parameters of the mathematical models that were obtained from a nonlinear fit of the experimental kinetic data to the models. Figs. 9–12 present experimental data on ion exchange kinetics and the results generated by the mathematical models. Based on the coefficients of determination shown in Table 5, the model that considered intraparticle diffusion as the limiting step of the overall mass transfer process best described the experimental data on ion exchange kinetics for the 'investigated systems (Ni^{2+}/Na^+ and Zn^{2+}/Na^+), once for Figure 12 also observed that the model (b) that considered intraparticle diffusion as the limiting step of the overall mass transfer process best described the experimental data on ion exchange kinetics.

Valverde et al. [29] determined intraparticle diffusion coefficients for Cu^{2+}, Cd^{2+}, Zn^{2+}, and H^+ ions in Amberlite IR 120 resin. The value obtained for Zn^{2+} was 1.49×10^{-11} m^2 s^{-1}. In the present work, using Eq. (38) and the values of K_S from Table 5, the following values of the intraparticle diffusion coefficient were obtained for Zn^{2+} ion: 1.10×10^{-12} m^2 s^{-1} for $C_0 = 0.5$ meq L^{-1} and 1.20×10^{-11} m^2 s^{-1} for $C_0 = 7.0$ meq L^{-1}. These values agree fairly well with that reported by Valverde et al. [29]. Thus, in the ion exchange process where Amberlite IR 120 resin is used as ion exchanger, the application of the LDF model appears to be a good alternative for process modeling. This approximation is valid for parabolic concentration profiles. A detailed description of the LDF model derivation is presented by CRUZ et al. [30].

5. Conclusion

Experimental data on ion exchange equilibrium was obtained for the binary (Ni^{2+}/Na^+ and Zn^{2+}/Na^+) and ternary ($Ni^{2+}/Zn^{2+}/Na^+$) systems using Amberlite IR 120 resin. Kinetic data on ion exchange for the binary system was also obtained. For the pH value obtained in the kinetics and equilibrium experiments for the binary systems, the predominant ionic forms in solution were Ni^{2+} and Zn^{2+} (near 100%). The model that considered intraparticle diffusion as the limiting step of the overall mass transfer process satisfactorily described the ion exchange kinetics. Equilibrium data was modeled using the ideal and non-ideal law of mass action, the latter best describing the equilibrium of binary systems. The non-ideal law of mass action model was capable of predicting the experimental data of equilibrium for the ternary system based on the parameters obtained for the binary systems (interaction parameters of Wilson's model and thermodynamic equilibrium constants).

References

[1] M.T. Veit, E.A. Silva, C.R.G. Tavares, M.R. Fagundes-Klen, G.C. Gonçalves, A.A. Seolatto, L.G.L. Vaz, Biosorption of nickel(II) ions by using chemically pretreated *Sargassum filipendula* biomass in a fixed bed column, World J. Microbiol. Biotechnol. 25 (2009) 1849–1856.
[2] M.R. Fagundes-Klen, M.T. Veit, C.E. Borba, R. Bergamasco, L.G.L. Vaz, E.A. Silva, Copper biosorption by biomass of marine alga: study of equilibrium and kinetics in batch system and adsorption/desorption cycles in fixed bed column, Water Air Soil Pollut. 213 (2010) 15–26.
[3] S. Kocaoba, Comparison of amberlite IR 120 and dolomite's performances for removal of heavy metals, J. Hazard. Mater. 147 (2007) 488–496.
[4] T. Shek, A. Ma, V.K.C. Lee, G. MCkay, Kinetics of zinc ions removal from effluents using ion exchange resin, Chem. Eng. J. 146 (2009) 63–70.
[5] M.J. Kumar, N.V. Nguyen, J.C. Lee, L. Jeong, J. Yoo, Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120, J. Hazard. Mater. 164 (2009) 948–953.
[6] C.E. Borba, E.A. Silva, S. Sporh, G.H.F. Santos, R. Guirardello, Ion exchange equilibrium prediction for the system Cu^{2+}–Zn^{2+}–Na^+, J. Chem. Eng. Data 55 (2010) 1333–1341.
[7] I. Lee, Y. Kuan, J. Chern, Equilibrium and kinetics of heavy metal ion exchange, J. Chinese Inst. Chem. Eng. 38 (2007) 71–84.

[8] M. Carmona, J. Warchol, A. Lucas, J.F. Rodriguez, Ion-exchange equilibria of Pb^{2+}, Ni^{2+}, and Cr^{3+} ions for H$^+$ on Amberlite IR-120 resin, J. Chem. Eng. Data 53 (2008) 1325–1331.

[9] B. Aliüz, V. Sevil, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater. 167 (2009) 482–488.

[10] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin, J. Colloid Interface Sci. 282 (2005) 20–25.

[11] P.G. Priya, C.A. Basha, V. Ramamurthi, S.N. Begun, Recovery and reuse of Ni(II) from rinsewater of electroplating industries, J. Hazard. Mater. 163 (2009) 899–909.

[12] Z. Zainol, M.J. Nicol, Ion-exchange equilibria of Ni^{2+}, Co^{2+}, Mn^{2+} and Mg^{2+} with iminodiacetic acid chelating resin Amberlite IRC 748, Hydrometallurgy 99 (2009) 175–180.

[13] J.L. Valverde, A. Lucas, M. González, J.F. Rodriguez, Ion-exchange equilibria of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Na$^+$ ions on the cationic exchanger Amberlite IR-120, J. Chem. Eng. Data 46 (2001) 1404–1409.

[14] L. Lin, R. 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.

[15] J.L. Valverde, A. Lucas, M. González, J.F. Rodriguez, Equilibrium data for the exchange of Cu^{2+}, Cd^{2+}, and Zn^{2+} ions for H$^+$ on the cationic exchanger Amberlite IR-120, J. Chem. Eng. Data 47 (2002) 613–617.

[16] R. Petrus, J.K. Warchol, Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems, Water Res. 39 (2005) 819–830.

[17] F.J. Alguacil, M. Alonso, L.J. Lozano, Chromium (III) recovery from waste acid solution by ion exchange processing using Amberlite IR-120 resin: batch and continuous ion exchange modeling, Chemosphere 57 (2004) 789–793.

[18] L. Lin, R. Juang, Ion-exchange kinetics of Cu(II) and Zn(II) from aqueous solutions with two chelating resins, Chem. Eng. J. 132 (2007) 205–213.

[19] R.S. Juang, S.H. Lin, T.Y. Wang, Removal of metal ions from the complexed solutions in fixed bed using a strong-acid ion exchange resin, Chemosphere 53 (2003) 1221–1228.

[20] I. Puigdomenech, HYDRA: Hydrochemical Equilibrium-Constant Database Software, Royal Institute of Technology, Sweden, 2004.

[21] L.A. Bromley, Thermodynamic properties of strong electrolytes in aqueous solutions, AIChE J. 19 (1973) 313–320.

[22] J.F. Zemaitis Jr., D.M. Clark, M. Rafal, N.C. Scrivner, Handbook of Aqueous Electrolyte Thermodynamics, American Institute of Chemical Engineers, New York, 1986.

[23] G.M. Wilson, Vapor–liquid equilibria XI. A new expression for the excess free energy of mixing, J. Am. Chem. Soc. 86 (1964) 127–130.

[24] J.A. Nelder, R. Mead, A simplex method for function minimization, Comput. J. 7 (1965) 308–315.

[25] M.A. Mehablia, D.C. Shallcross, G.W. Stevens, Prediction of multicomponent ion exchange equilibria, Chem. Eng. Sci. 49 (1994) 2277–2286.

[26] R.M. Allen, P.A. Addison, A.H. Dechapunya, The characterization of binary and ternary ion exchange equilibria, Chem. Eng. J. 40 (1989) 151–158.

[27] E. Glueckauf, J.J. Coates, Theory of chromatography part IV: the influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation, J. Chem. Soc. (1947) 1315–1321.

[28] S.I. Sandler, Chemical Engineering Thermodynamics, third ed., John Wiley & Sons, NewYork, 1999.

[29] J.L. Valverde, A. Lucas, M. Carmona, M. González, J.F. Rodríguez, A generalized model for the measurement of effective diffusion coefficients of heterovalent ions in ion exchangers by the zero-length column method, Chem. Eng. Sci. 59 (2004) 71–79.

[30] P. Cruz, F.D. Magalhães, A. Mendes, Generalized linear driving force approximation for adsorption of multicomponent mixtures, Chem. Eng. Sci. 61 (2006) 3519–3531.