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Ion exchange recovery of Ni(II) from simulated electroplating waste solutions containing anionic ligands

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Abstract

Ion exchange is widely used for the recovery and removal of metals from process and waste streams in chemical process industries. The Na-form of strong-acid Purolite NRW-100 resin was used to recover Ni(II) from a simulated electroplating waste solution containing $NiSO_4$, NH_4Cl, NaH_2PO_4, and citrate. A set of mass balance equations that take into account possible aqueous complexation reactions was used to establish the pH diagram of Ni(II) species in the presence of anionic ligand citrate or phosphate. Experiments were performed as a function of initial solution pH (0.5–6.0), initial concentration of Ni(II) (0.85–11.9 mol/m^3), and temperature (15–45 °C). It was shown that the amount of Ni(II) exchanged leveled off when the equilibrium pH was higher than around 2.5. The exchange isotherms obtained at various equilibrium pH values were well fitted by the Langmuir equation. The enthalpy of Ni(II) exchange was also evaluated based on the Langmuir constant. Finally, the kinetics of the present ion exchange process was analyzed.
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Keywords: Cation exchange; Ni(II); Equilibrium; Kinetics; Simulated electroplating solutions; Anionic ligands

1. Introduction

Most of metal finishing or electroplating solutions contain water-soluble anionic ligands due to their three-fold function: to keep metals in solution, to dissolve metal compounds, and to affect the chemical reactivity of metal ions [1–3]. Of these ligands, polycarboxylic acids such as citrate, oxalate, and tartrate as well as phosphoric acids are often employed, although they offer smaller complex stability than aminopolycarboxylic acids such as ethylenediaminetetraacetic acid and nitrilotriacetic acid [2].

For treatment of metal-bearing solutions, the presence of anionic ligands can make common chemical precipitation such as hydroxide and sulfide less effective because of the formation of negatively charged species [1]. Alternative methods are desired, which strongly depend on the particular ligands and metals as well as their concentrations. For dilute solutions, reverse osmosis, solvent extraction, adsorption, and ion exchange could be used [3–7]. In general, reverse osmosis has high operating and maintenance costs and is subject to fouling. Solvent extraction has high recovery capacity and selectivity but often suffers from solvent loss and the problems of phase separation. Activated carbon adsorption is not effective for this subject although it has been widely used for removal of organic contaminants [4]. Thus, ion exchange appears to be a promising candidate for the treatment of such streams in chemical process industries [5–7].

When the anionic ligands have strong complexing ability or are in large excess of metal ions in solution, chelating exchangers [8] or common anion-exchange resins [9–11] can be used because the metallic species are negatively charged. Otherwise, commercial cation-exchange resins are the alternative of choice. The goal of this paper was to investigate the exchange phenomena of metal ions from dilute solutions in the presence of anionic ligands including citrate and phosphate with a common strong-acid resin. In this work, Ni(II) was selected as the target metal due to its wide use in many electroplating industries [3,6,7,10–12]. Both equilibrium and kinetics of ion exchange were investigated to determine the

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Nomenclature

C_e	liquid-phase Ni(II) concentration at equilibrium (mol/m^3)
C_t	liquid-phase Ni(II) concentration at time t (mol/m^3)
C_0	initial liquid-phase Ni(II) concentration (mol/m^3)
H_3L	citric acid
k_1	forward rate constant (1/h)
k_2	reverse rate constant (kg/(m^3 h))
K_D	distribution constants defined in Eq. (26) (m^3/kg)
K_i	equilibrium constants defined in Eqs. (2)–(8) and (13)–(17) (molar basis)
K_L	Langmuir constant (m^3/mol)
m	dose of the dry resins (kg/m^3)
q_e	amount of Ni(II) exchanged at equilibrium (mol/kg)
q_{sat}	saturated amount of Ni(II) exchanged at a given equilibrium pH (mol/kg)

isotherms and kinetic parameters on a macroscopic basis. All experiments were performed at different initial concentrations of metal ions (0.85–11.9 mol/m^3), initial aqueous pH values (0.5–6.0), and temperatures (15–45 °C).

2. Materials and methods

2.1. Resins and reagents

The strong-acid cation exchange resin Purolite NRW-100 with sulfonic acid –SO_3H group was used in this work. The physical and chemical properties of the resins are listed in Table 1. Prior to use, the resins were washed with NaOH (1 mol/dm^3), HCl (1 mol/dm^3), and *n*-hexane in sequence to remove possible organic and inorganic impurities, and were washed with deionized water (Millipore Milli-Q) three times. The resins were finally converted to the Na^+ form by flushing the column with 1 mol/dm^3 of NaOH solution for 12 h. They were washed with deionized water until the resulting water became neutral, and were dried in a vacuum oven at 50 °C overnight.

Table 1
Physical and chemical properties of the Purolite NRW-100 resin

Properties	Description or values
Matrix	Polystyrene-divinyl benzene, gel type
Degree of cross-linking	Not available
Functional group	Sulfonic acid, $-SO_3^-$
Ionic form	H^+ (>99.9%)
Exchange capacity (equiv/kg of dry resin)	4.5
Moisture content (%)	50–55
Particle size (mm)	0.425–1.2
Specific gravity	1.20

Analytical reagent grade $NiSO_4$, NaH_2PO_4, NH_4Cl, trisodium salt of citric acid, and other inorganic chemicals such as HCl and NaOH were purchased from Merck Co. They were used without further purification.

2.2. Experimental procedures

In ion exchange equilibrium experiments, an aliquot of the dry resins (0.1 g) and 100 cm^3 of the aqueous solution were placed in a 125-cm^3 glass-stoppered flask, and were shaken using a shaker at 120 rpm for 24 h (Firstek B603, Taiwan). The aqueous solutions always consisted of a fixed amount of NaH_2PO_4 (1.1 mol/m^3) and NH_4Cl (11.2 mol/m^3), as well as a varying, equimolar amount of $NiSO_4$ (C_0) and citrate (0.85–11.9 mol/m^3). The initial solution pH was adjusted to be in the range 0.5–6.0 by adding small amounts of 0.1 mol/dm^3 of HCl or NaOH. The temperature of water bath was controlled in the range 25–45 °C. Preliminary tests had shown that the exchange reactions studied were complete within 6 h. After equilibrium, the aqueous-phase concentrations of Ni(II) and Na(I) were determined using an atomic absorption spectrophotometer (Varian 220FS). The equilibrium pH value was measured with a pH meter (Horiba F-23, Japan). The resin-phase concentration of Ni(II) at equilibrium, q_e (mol/kg), was obtained according to

$$q_e = \frac{C_0 - C_e}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium metal concentrations (mol/m^3) in the solution, respectively, and m is the dose of the dry resins (kg/m^3). In this work, m always equals 1 kg/m^3.

For contact-time experiments, the procedures were essentially the same as those described in equilibrium experiments except that the aqueous samples were taken at preset time intervals. The solution contained 1.1 mol/m^3 of NaH_2PO_4, 11.2 mol/m^3 of NH_4Cl, 5.1 mol/m^3 of $NiSO_4$ (C_0), and 5.1 mol/m^3 of trisodium citrate. The temperature was maintained at 25 °C. The concentrations of Ni(II) in the solutions were measured accordingly. Each experiment was at least duplicated under identical conditions. The reproducibility of the measurements was within 6% (mostly 3%).

3. Results and discussion

3.1. Effect of pH and initial concentration on ion exchange

Figs. 1 and 2 show the effects of equilibrium pH (pH_{eq}) and the initial Ni(II) concentration on the amount of Ni(II) exchanged (q_e). Under the Ni(II) concentration range studied, it is found that the q_e value increases with increasing pH_{eq}

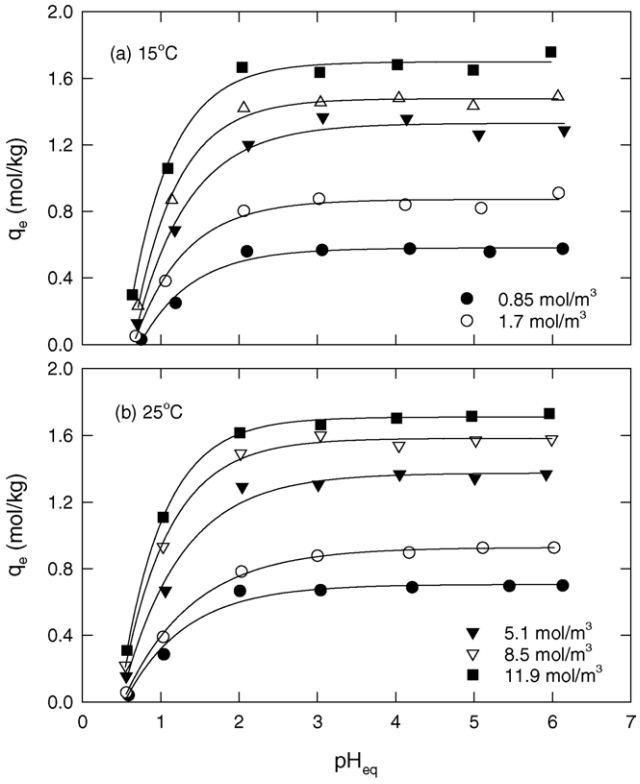

Fig. 1. Effect of the initial metal concentration and equilibrium pH value on the amount of Ni(II) exchanged at 15 and 25 °C.

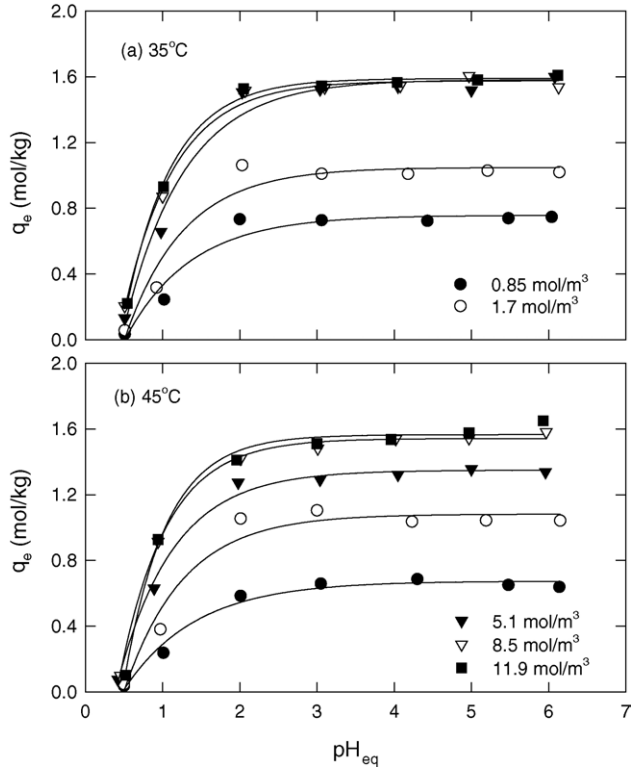

Fig. 2. Effect of the initial metal concentration and equilibrium pH value on the amount of Ni(II) exchanged at 35 and 45 °C.

and reaches a plateau when pH_{eq} exceeds a threshold (around 2.5). The low q_e value obtained at low pH_{eq} is caused by competitive exchange of H^+ and Ni^{2+} ions with the Na form of the resins.

In the absence of ion exchange resins, the distribution of Ni(II) species at different solution pH values can basically be calculated from a set of mass balance equations. In $NiSO_4$–trisodium citrate system, the following complexation reactions are considered.

$$Na^+ + L^{3-} \Leftrightarrow NaL^{2-}, \quad K_1 \tag{2}$$

$$Ni^{2+} + L^{3-} \Leftrightarrow NiL^-, \quad K_2 \tag{3}$$

$$Ni^{2+} + H^+ + L^{3-} \Leftrightarrow NiHL, \quad K_3 \tag{4}$$

$$Ni^{2+} + 2H^+ + L^{3-} \Leftrightarrow NiH_2L^+, \quad K_4 \tag{5}$$

$$H^+ + L^{3-} \Leftrightarrow HL^{2-}, \quad K_5 \tag{6}$$

$$2H^+ + L^{3-} \Leftrightarrow H_2L^-, \quad K_6 \tag{7}$$

$$3H^+ + L^{3-} \Leftrightarrow H_3L, \quad K_7 \tag{8}$$

In this case, the following set of mass balance equations is established at equilibrium.

$$[Ni^{2+}]_{tot} = [Ni^{2+}] + [NiL^-] + [NiHL] + [NiH_2L^+] \tag{9}$$

$$[L^{3-}]_{tot} = [L^{3-}] + [NaL^{2-}] + [NiL^-] + [NiHL] + [NiH_2L^+] + [HL^{2-}] + [H_2L^-] + [H_3L] \tag{10}$$

$$[H^+]_{tot} = [H^+] + [NiHL] + 2[NiH_2L^+] + [HL^{2-}] + 2[H_2L^-] + 3[H_3L] \tag{11}$$

$$[Na^+]_{tot} = [Na^+] + [NaL^{2-}] \tag{12}$$

The four unknowns ($[Ni^{2+}]$, $[Na^+]$, $[H^+]$, and $[L^{3-}]$) are obtained by solving the system of Eqs. (9)–(12) using Mathematica, version 3.0 at given conditions.

On the other hand, the following reactions must be covered in $NiSO_4$–NaH_2PO_4 system.

$$Na^+ + H^+ + PO_4^{3-} \Leftrightarrow NaHPO_4^-, \quad K_8 \tag{13}$$

$$H^+ + PO_4^{3-} \Leftrightarrow HPO_4^{2-}, \quad K_9 \tag{14}$$

$$2H^+ + PO_4^{3-} \Leftrightarrow H_2PO_4^-, \quad K_{10} \tag{15}$$

$$3H^+ + PO_4^{3-} \Leftrightarrow H_3PO_4, \quad K_{11} \tag{16}$$

$$Ni^{2+} + H^+ + PO_4^{3-} \Leftrightarrow NiHPO_4, \quad K_{12} \tag{17}$$

The following set of mass balance equations holds at equilibrium.

$$[Ni^{2+}]_{tot} = [Ni^{2+}] + [NiHPO_4] \tag{18}$$

$$[H^+]_{tot} = [H^+] + [NaHPO_4^-] + [HPO_4^{2-}] + 2[H_2PO_4^-] + 3[H_3PO_4] + [NiHPO_4] \tag{19}$$

Table 2
Values of the equilibrium constants at 25 °C and different ionic strengths [13,14]

Equilibrium constant, K_i	Ionic strength, 0 M	Ionic strength, 0.1 M
K_1 (M^{-1})	2.51×10^{1}	5.62×10^{0}
K_2 (M^{-1})	5.01×10^{6}	1.51×10^{5}
K_3 (M^{-2})	3.16×10^{10}	8.51×10^{8}
K_4 (M^{-3})	7.94×10^{12}	4.90×10^{11}
K_5 (M^{-1})	2.51×10^{6}	4.37×10^{5}
K_6 (M^{-2})	1.45×10^{11}	9.77×10^{9}
K_7 (M^{-3})	1.95×10^{14}	7.76×10^{12}
K_8 (M^{-2})	3.16×10^{13}	1.35×10^{12}
K_9 (M^{-1})	2.24×10^{12}	3.31×10^{11}
K_{10} (M^{-2})	3.55×10^{19}	1.70×10^{18}
K_{10} (M^{-3})	5.01×10^{21}	1.35×10^{20}
K_{12} (M^{-2})	2.51×10^{15}	4.17×10^{13}

$$[PO_4^{3-}]_{tot} = [PO_4^{3-}] + [NaHPO_4^{-}] + [HPO_4^{2-}] + [H_2PO_4^{-}] + [H_3PO_4] + [NiHPO_4] \quad (20)$$

$$[Na^{+}]_{tot} = [Na^{+}] + [NaHPO_4^{-}] \quad (21)$$

Similarly, the four unknowns ($[Ni^{2+}]$, $[Na^{+}]$, $[H^{+}]$, and $[PO_4^{3-}]$) are obtained by solving the system of Eqs. (18)–(21) at a given conditions.

The equilibrium constants $K_1 \sim K_{12}$ at 25 °C and an ionic strength of 0 M [13] and 0.1 M [14] are complied in Table 2. Evidently, citrate (L^{3-}) readily forms stable complexes with Ni^{2+} in a 1:1 molar ratio and is a stronger ligand than phosphate with Ni^{2+} ions in aqueous solution. Two typical solutions are exemplified; one contains 5.1-mol/m^3 $NiSO_4$ and 5.1-mol/m^3 trisodium citrate (ionic strength, 51 mol/m^3), and the other contains 5.1-mol/m^3 $NiSO_4$ and 1.1-mol/m^3 NaH_2PO_4 (ionic strength, 27 mol/m^3). In this work, the K_i's values are further corrected with the ionic strength by interpolation through the linear relationship between the logarithm of K_i value and the reciprocal of the square root of ionic strength [15].

In equimolar Ni(II)–citrate solution, free Ni^{2+} ions dominate at pH < 2.3 and the species NiL^{-} are absolutely dominant (>95%) at pH > 3.5 (Fig. 3a). Such a pH dependence is slightly different from that observed in an equimolar Cu(II)–citrate system [16]; in which the dominant species are free Cu^{2+} ions at pH < 4.0 and the species CuL^{-} at pH > 6.8. Between pH 4.0 and 6.8, the neutral species CuHL dominates. On the other hand, free Ni^{2+} ions always dominate in Ni(II)–phosphate solution under the pH ranges studied. Therefore, the present findings about pH effect on q_e values (Figs. 1 and 2) likely imply that the sulfonate groups of the resins strongly compete with citrate in the solution for reacting with Ni^{2+} ions, thereby altering the chemical equilibrium between Ni^{2+} ions and citrate in the solution. Of course, such a competitive effect increases with increasing pH and eventually reaches a limit beyond a threshold pH.

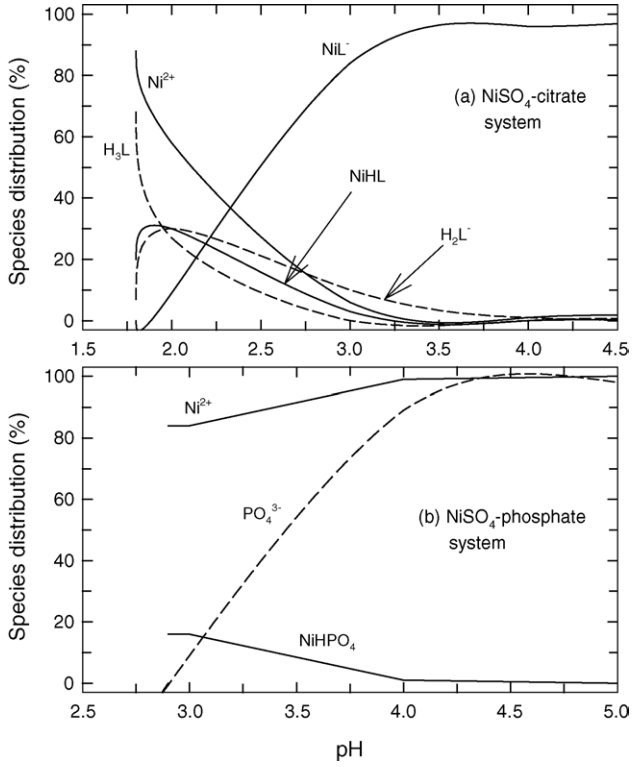

Fig. 3. The pH diagram of species distribution in the systems of (a) 5.1-mol/m^3 $NiSO_4$ and 5.1-mol/m^3 trisodium citrate, and (b) 5.1-mol/m^3 $NiSO_4$ and 1.1-mol/m^3 NaH_2PO_4 at 25 °C.

In practice, Tare et al. [8] used an ion exchanger, Chelex-100, to recover Cu^{2+}, Ni^{2+}, and Pb^{2+} from synthetic water containing a total metal concentration of 4.2 mol/m^3 and mixtures of EDTA, citrate, and tartrate (total ligand concentration, 7.3 mol/m^3). They also observed that the rates of metal exchange depended not only on the rate-limiting steps (film diffusion, particle diffusion, or chemical reaction), but also on the rate of complex formation or destruction in solutions and the competition for soluble ligands or exchange sites among various metal ions.

3.2. Macroscopic exchange equilibrium model

Figs. 4 and 5 show the isotherms of Ni(II) exchange obtained at different fixed pH_{eq} values and temperatures. On a macroscopic basis, these data can be correlated by the common Langmuir equation given by [17]

$$q_e = \frac{q_{sat} K_L C_e}{1 + K_L C_e} \quad (22)$$

where K_L is the Langmuir constant (m^3/mol) and q_{sat} is the saturated amount of metal exchanged at a given equilibrium pH (mol/kg). The parameters K_L and q_{sat} can be obtained from a plot of $1/q_e$ versus $1/C_e$ (Table 3). The solid curves shown in Figs. 4 and 5 are calculated from the Langmuir equation (correlation coefficient, $R^2 > 0.9574$).

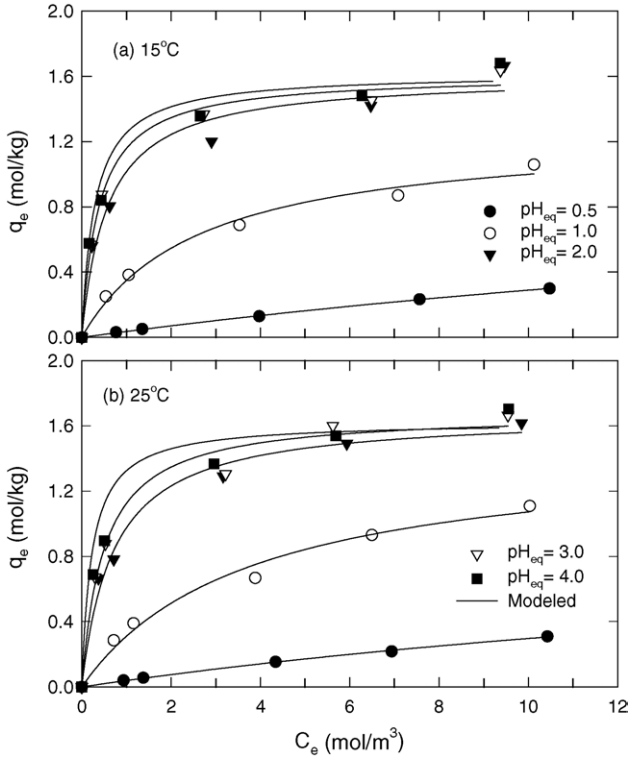

Fig. 4. Exchange isotherms of Ni^{2+} at various equilibrium pH values and at 15 and 25 °C. (The solid curves are predicted by the Langmuir equation.)

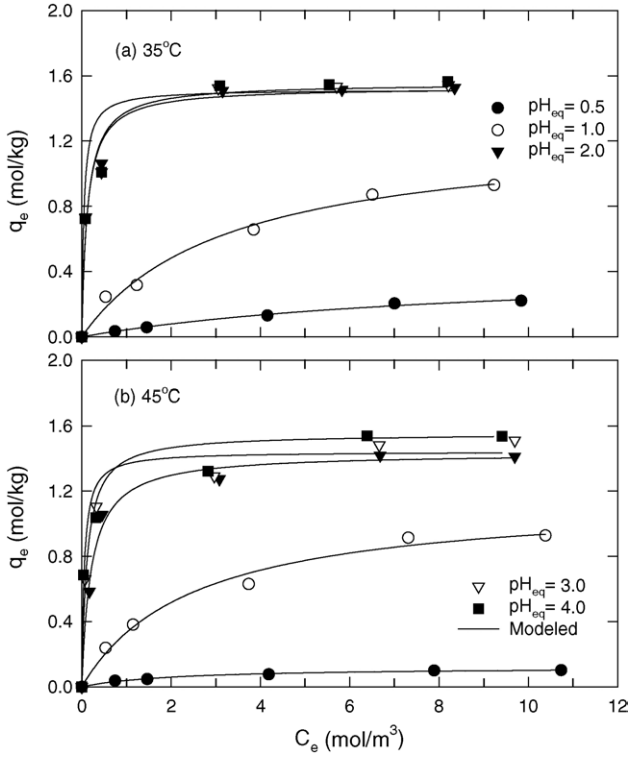

Fig. 5. Exchange isotherms of Ni^{2+} at various equilibrium pH values and at 35 and 45 °C. (The solid curves are predicted by the Langmuir equation.)

Table 3
Parameters of the Langmuir equation for the exchange of Ni(II) with the Na form of NRW-100 resin

pH$_{eq}$	q_{sat} (mol/kg)				K_L (m^3/mol)			
	15 °C	25 °C	35 °C	45 °C	15 °C	25 °C	35 °C	45 °C
0.5	1.18	1.06	0.47	0.16	0.04	0.14	0.31	0.60
1.0	1.33	1.19	1.09	1.06	0.31	0.46	0.83	0.95
2.0	1.75	1.69	1.56	1.53	0.95	1.39	2.18	3.28
3.0	1.77	1.72	1.60	1.58	1.40	1.85	3.16	4.25
4.0	1.77	1.72	1.61	1.59	1.88	2.94	4.89	6.31

It is found that a rise of temperature leads to an increase of K_L but a decrease of q_{sat}. On the other hand, both K_L and q_{sat} increase with increasing pH$_{eq}$. At a pH$_{eq}$ of 4.0, for example, the q_{sat} value is 1.72 mol/kg (or 3.44 equiv/kg) at 25 °C, which is smaller than the resin capacity (4.5 equiv/kg). The remaining exchange sites on the resins are mostly occupied by Na^+ ions.

The representation of ion exchange equilibrium data by "adsorption" isotherm equations is simple and acceptably good although their parameters q_{sat} and K_L would change with the solution environment particularly with pH$_{eq}$ value [17]. This is widely done because such simplified type of equilibrium expression makes the subsequent dynamic modeling in fixed bed operations more convenient [18].

3.3. Thermodynamics of ion exchange

Now, we can evaluate the enthalpy of Ni(II) exchange according to the van't Hoff equation:

$$\frac{d(\ln K_L)}{d(1/T)} = -\frac{\Delta H_{ads}}{R} \quad (23)$$

Fig. 6 shows the linear relationships (correlation coefficient $R^2 > 0.9356$) at various pH$_{eq}$ values, and Table 4 lists the calculated enthalpies. The endothermic nature of ion exchange process has also been reported previously [10,19,20]. For example, the enthalpies of 1.73, 1.83, and 1.64 kJ/mol have been obtained for the exchange of Cu–,

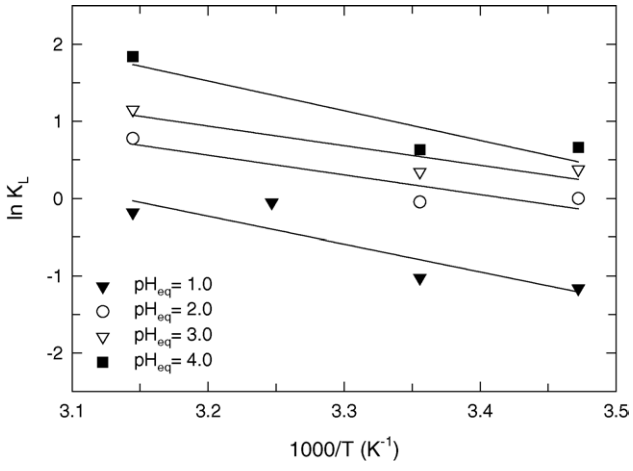

Fig. 6. The van't Hoff plot of the Langmuir equilibrium constant K_L.

Table 4
The enthalpy of Ni(II) exchange with the Na form of NRW-100 resin calculated based on different Langmuir constants

pH_{eq}	ΔH_{ads} (kJ/mol)
1.0	29.9
2.0	26.3
3.0	26.1
4.0	32.1

Co–, and Ni–EDTA chelates with Amberlite IRA-68 resins, respectively, according to the temperature variations of chemical equilibrium constants [10]. Zagorodni et al. [19] have studied the exchange of Cu^{2+} from sulfate solution with the Zn form of Amberlite IRC-718 resin in the temperature range15–75 °C. They also obtained an enthalpy change of 2.32 kJ/mol.

It is noticed that the ΔH_{ads} values are within 26.1–32.1 kJ/mol. According to the concept of the Langmuir model, the present ion exchange process should be a type of physisorption because the enthalpy of physisorption is usually in the region of 20 kJ/mol and that of chemisorption is in the region of 200 kJ/mol [21].

The positive ΔH can be understood because the conventional exchange or adsorption process corresponds to the results of two simple processes: (i) exchange of the molecules of solvent (water) previously adsorbed, and (ii) exchange of the solute molecules. Each molecule of metal ions has to displace more than one molecules of water. The net result corresponds to an endothermic process [22]. Another explanation would be that the overall process is virtually a combination of proton desorption and Ni^{2+} adsorption, because the enthalpy change for proton adsorption onto ion exchangers was reported to be −30 to −39 kJ/mol [23].

3.4. Kinetics of ion exchange

An attempt was also made to analyze the kinetics of the present ion exchange process. Simply put, the ion exchange reaction between Ni^{2+} and the Na-form resin can be expressed by

$$Ni^{2+} + 2\overline{NaR} \Leftrightarrow \overline{NiR_2} + 2Na^+$$

It is considered that the exchange reaction follows the pseudo-first-order reversible kinetics [24]; that is,

$$\frac{d[Ni^{2+}]_t}{dt} = k_1[Ni^{2+}]_t - k_2[\overline{NiR_2}]_t \quad (24)$$

where k_1 and k_2 are the forward and reverse rate constants, respectively. If the concentration terms refer to the liquid phase, Eq. (24) can be rewritten as

$$\frac{dC_t}{dt} = k_1 C_t - k_2 \frac{C_0 - C_t}{m} \quad (25)$$

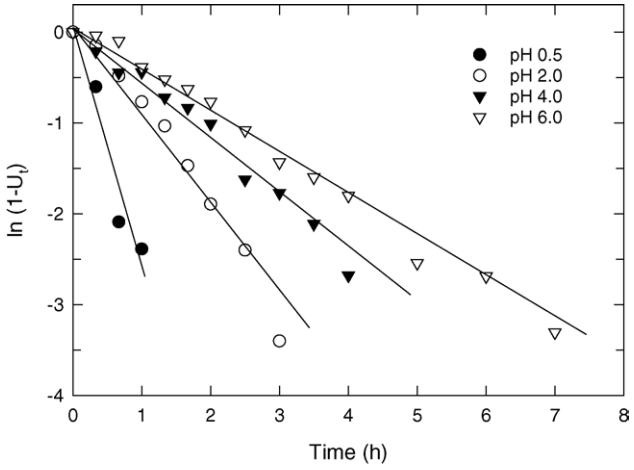

Fig. 7. Typical analysis of the kinetics of the present ion exchange process at 25 °C (m = 1 kg/m^3, C_0 = 5.1 mol/m^3).

At equilibrium (i.e., dC_t/dt approaches zero), we have

$$K_D = \frac{(C_0 - C_e)/m}{C_e} = \frac{k_1}{k_2} \quad (26)$$

where K_D is the exchange distribution constant (m^3/kg). Combining Eqs. (25) and (26) yields

$$\frac{dC_t}{dt} = -\left(k_1 + \frac{k_2}{m}\right)(C_e - C_t) \quad (27)$$

Integrating Eq. (27) with the conditions: $C_t = C_0$ at $t = 0$ and $C_t = C_t$ at $t = t$, we have

$$\ln\left[\frac{C_e - C_t}{C_e - C_0}\right] = -\left(k_1 + \frac{k_2}{m}\right)t \quad (28)$$

or, in the form of

$$\ln(1 - U_t) = -\left(k_1 + \frac{k_2}{m}\right)t \quad (29)$$

where U_t is the fractional attainment to equilibrium defined by

$$U_t = \frac{C_0 - C_t}{C_0 - C_e} \quad (30)$$

Evidently, the linear plot of $\ln(1 - U_t)$ versus t gives the value of $k_1 + (k_2/m)$, as typically shown in Fig. 7. This verifies the validity of the pseudo-first-order reversible kinetics. Because the ratio k_1/k_2 can be determined directly from the equilibrium experiments according to Eq. (26), the individual rate constants k_1 and k_2 can be obtained (Table 5). It is

Table 5
Rate constants for the exchange of Ni(II) with the Na form of NRW-100 resin at 25 °C (m = 1 kg/m^3, C_0 = 5.1 mol/m^3)

pH	$k_1 + (k_2/m)$ (1/h)	k_1 (1/h)	k_2 (kg/(m^3 h))
0.5	2.60	0.57	2.03
2.0	1.26	0.40	0.86
4.0	0.71	0.25	0.46
6.0	0.51	0.18	0.33

found that both k_1 and k_2 values decrease with increasing pH value. This means that the competitive exchange of H^+ on the resins enhances the exchange of Ni^{2+} ions (kinetically synergistic effect). According to Eq. (2), the ratio of k_1/k_2, called exchange distribution coefficient K_D (Eq. (26)), equals the product of q_{sat} and the Langmuir constant K_L only if $K_L C_e \ll 1$. This constraint is not wholly satisfied in this work. Thus, it is difficult to determine the values of k_1 and k_2 from the Langmuir constant K_L.

Moreover, the (k_2/m) value is larger than k_1 value, indicating that the forward reaction is not favored. Different trends have been reported in the exchange of Co(II) from nitrate solution using the H form of sulfonic acid resin Amberlite IRN-77 [24]. The present results likely ascribe to the presence of anionic ligands in the solution, which retard with the resins for attracting Ni^{2+} ions.

4. Conclusions

The ion exchange of Ni(II) between the Na form of Purolite NRW100 resin and simulated electroplating waste solution has been studied in the temperature range 15–45 °C. The Langmuir equation gave a good representation of the equilibrium data (correlation coefficient, $R^2 > 0.9574$), although their parameters q_{sat} and K_L would change with solution pH. The van't Hoff plot of K_L yielded an enthalpy change (ΔH_{ads} = 26.1–32.1 kJ/mol) in the pH range 1.0–4.0. This positive enthalpy change was likely due to the fact that the overall ion exchange process was a combination of H^+ desorption and Ni^{2+} exchange. The present Ni^{2+} exchange onto the Na-form strong-acid resin followed the pseudo-first-order reversible kinetics. Moreover, the presence of anionic ligands such as citrate and phosphate in solution did not favor the forward exchange reaction.

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