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Removal of Ni(II) and Co(II) ions from acidic solutions by Lewatit TP-260 resin

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ABSTRACT

This paper examines Ni(II) and Co(II) adsorption from an aqueous sulfate solution onto Lewatit TP-260 ion exchange resin, and the later desorption of these ions. The influence on metals adsorption of contact time, the pH of the metal-containing solution, the initial concentration of metals in the solution, and the amount of resin was examined in batch experiments. The coefficients of adsorption under different experimental conditions were then determined. Batch experiments were also performed to examine desorption or elution at different volumes/resin ratios and HCl (eluant) concentrations. Adsorption experiments were also performed in minicolumns to study the performance of the resin under conditions of continuous use. Different flow rates for the inlet metals-bearing solution and different resin weights were tested in the adsorption phase (performed at pH 3.1). The results of the batch experiments showed that the resin is able of adsorbing both metals under a range of conditions. The mechanism that best described this adsorption varied depending on the metal and experimental conditions used. The results of the continuous experiments showed that the nickel and cobalt adsorption is increased with increasing the resin weight and decreasing the flow rate of the metals-bearing solution.

Keywords: Adsorption; Desorption; Ni(II); Co(II); Lewatit TP-260 resin

1. Introduction

Interest in the recovery of Ni and Co from waste solutions has increased in recent years, a consequence of the high industrial demand for these elements, though chemical similarities between both elements make somewhat difficult their separation. Including in the various separations technology used in this role, ion exchange or adsorption processes are widely used in the recovery of various metals particularly from dilute solutions [1–5].

Ion exchange resins have also been widely used in the adsorption of Ni and Co bearing solutions [6–13]. Ion exchange resins used in this role can be broadly classified into two main groups, being this classification made by considering the type of reactive groups associated with the resin: (i) strong and weak cation exchange resins, containing sulfonic and carboxylic active groups and (ii) exchange resins containing chelating groups, i.e., iminodiacetic and aminophosphonic groups.

The present work examines, in batch experiments, the adsorption of Ni(II) and Co(II) from an aqueous sulfate solution onto a Lewatit TP-260 exchange resin under different conditions of aqueous pH, initial metals concentration, contact time, and the amount of resin used in the exchange process. The adsorption kinetics coefficients and adsorption mechanisms for both metals were then determined at these different conditions. Continuous adsorption experiments were also performed to determine the influence of weighed resin and the flow rate of the metals-containing solution in the metals load onto the resin.

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2. Materials and methods

All chemicals used in the present work were of analytical reagent grade. The concentrations of Ni(II) and Co(II) in aqueous solution were determined using a Perkin Elmer 1100B atomic absorption spectrometer (AAS). pH values were monitored using an Oakton 20 pH-meter. The ion exchange resin used was Lewatit TP-260, a macroporous cation exchange resin based on a cross-linked polystyrene matrix containing aminomethylphosphonic acid groups (Table 1).

2.1. Batch experiments

Different resin weights (1–4 g) were brought into contact for different lengths of times (0–180 min) with 200 mL of an aqueous sulfate solution containing Ni(II) and Co(II) (0.05 and 0.1 g/L for both) in the 1–5 pH range, in a glass reactor at room temperature and mechanical stirred via an impeller. The residual Ni(II) and Co(II) concentrations in the aqueous solution following each experiment were measured by AAS. Metal uptake onto the resin was calculated from the residual concentrations of Ni(II) and Co(II). All reactions were stirred at 1,000 min^{-1}, since previous experiments had shown that at this stirring speed, a maximum in metals uptake were achieved, and thus a minimum in the thickness of the aqueous boundary layer is reached [5].

To determine the possible adsorption or exchange mechanism, i.e., the film diffusion-controlled process, the particle diffusion-controlled process, or the moving boundary process, was obeyed under each set of conditions; the following equations were used:

$$\text{Film diffusion-controlled process: } \mathrm{Log}(1 - F) = -kt \quad (1)$$

$$\text{Particle diffusion-controlled process: } \mathrm{Log}(1 - F^2) = -kt \quad (2)$$

$$\text{Moving boundary process: } 3 - 3(1 - F)^{2/3} - 2F = kt \quad (3)$$

where *F* represents the fractional approach to equilibrium; *k* the kinetic coefficient of adsorption (or rate constant) and *t* the equilibrium time. The value of *F* with respect to Ni(II) and Co(II) was determined as follows:
for Ni(II):

$$F = \frac{[\mathrm{Ni}]_0 - [\mathrm{Ni}]_t}{[\mathrm{Ni}]_0 - [\mathrm{Ni}]_e} \quad (4)$$

for Co(II):

$$F = \frac{[\mathrm{Co}]_0 - [\mathrm{Co}]_t}{[\mathrm{Co}]_0 - [\mathrm{Co}]_e} \quad (5)$$

where $[\mathrm{Ni}]_0$ and $[\mathrm{Co}]_0$ are the initial concentrations of nickel and cobalt in the aqueous solution; $[\mathrm{Ni}]_t$ and $[\mathrm{Co}]_t$ are their concentrations at an elapsed time; and $[\mathrm{Ni}]_e$ and $[\mathrm{Co}]_e$ are the equilibrium concentrations for the ions in the aqueous solution.

The diffusion coefficients values were also estimated for the film diffusion-controlled and particle diffusion-controlled process, using the following relationships:

$$K = 3\,Df\,C_0/(r_0\,\delta\,\mathrm{Cab}) \text{ (film diffusion-controlled process)} \quad (6)$$

$$K = (Dp\,\pi^2)/(r_0)^2 \text{ (particle diffusion-controlled process)} \quad (7)$$

where *Df* and *Dp* represent the diffusion coefficient in the film diffusion-controlled and particle diffusion-controlled processes, respectively; r_0 is the mean resin particle radius (0.05 cm); C_0 is the initial ion concentration in the solution; Cab is the adsorbed ion concentration at time t_{50} (i.e., when 50% of adsorption equilibrium is achieved); and δ is the film thickness (10^{-3} cm).

Desorption batch experiments were performed using 10 or 20 mL of 4 or 8 M HCl, aqueous solutions containing Ni(II) and Co(II) ions (0.05 g/L for each), and a resin weight of 1 g (containing a known quantity of adsorbed Ni(II) and Co(II)) for a period of up to 30 min, at room temperature. The Ni(II) and Co(II) concentrations of the eluate were determined by AAS.

2.2. Continuous experiments

Continuous adsorption experiments were performed in minicolumns at pH 3.1 and metals concentrations of 0.01 g/L, using resin loads in the column (1, 2, or 3 g), and different aqueous solution flow rates (3, 6, and 12 cm^3/min). The exchange resin was loaded into the column (nominal capacity 5 mL, fitted with 20 µm polyethylene bed support), and the aqueous solution containing the Ni(II) and Co(II) ions passed downstream through the resin bed using a peristaltic pump. The outlet solution from the column was directed to the fraction collector. Fractions were collected at elapsed times, and the Ni(II) and Co(II) concentrations were determined by AAS.

Table 1
Characteristics of Lewatit TP-260 ion exchange resin

Polymer matrix	Polystyrene
Functional group	Aminomethylphosphonic acid
Ionic form	Di–Na$^+$
Bead size	0.4–1.25 mm
Max. operating temperature	110°C
Effective size	Around 0.55 mm
Density	1.2 g.mL^{-1}

3. Results and discussion

3.1. Batch experiments: Ni(II) and Co(II) adsorption

The reactions for Ni(II) and Co(II) uptake onto a resin, such as Lewatit TP-260, can be described by the following equations, which resembled well to a cation exchange process:

$$\mathrm{Ni}^{2+}_{aq} + 2\mathrm{R}^-\mathrm{Na}^+ \rightarrow \mathrm{R}^-_2\mathrm{Ni}^{2+} + 2\mathrm{Na}^+_{aq} \quad (8)$$

and

$$Co^{2+}_{aq} + 2R^{-}Na^{+} \rightarrow R_2^{-}Co^{2+} + 2Na^{+}_{aq} \tag{9}$$

where R refers to the resin matrix, and Na^+ the exchangeable ion. The ions loaded onto the resin can be desorbed or eluted by the use of HCl solutions.

3.1.1. Influence of the aqueous solution pH on the fractional approach to equilibrium

Fig. 1 shows the effect of the aqueous pH on the *F* value for Ni(II) and Co(II) uptake at different contact times. The metal concentration was of 0.05 g/L (each) in the aqueous solution, and the resin weight was of 2 g. The adsorption equilibrium was reached at about 30 min, after which the *F* values for both ions were virtually the same over the pH range 1.9–4.1. Table 2 shows the concentration of Ni(II) and Co(II) in the resin when the adsorption equilibrium was reached (30 min) at the different pH values tested.

3.1.2. Influence of initial concentration of metal ions on the fractional approach to equilibrium

Fig. 2 shows the effect of the initial Ni(II) and Co(II) concentration (0.05 and 0.1 g/L) on the value of *F* for these metals at different contact times, at a pH of 3.1 and using 2 g of resin.

Metal uptake onto the resin was faster over the first 30 min of contact, and after 50 min, the adsorption equilibrium was reached. Over 90% of adsorption occurred in the first 30 min for every metal concentrations were tested. It had been reported [14] a similar behavior in the adsorption of Cd(II) by Lewatit TP-260, although for Cd(II) the adsorption equilibrium was reached at times exceeding 2 h when an initial Cd(II) concentration of 0.025 g/L was used.

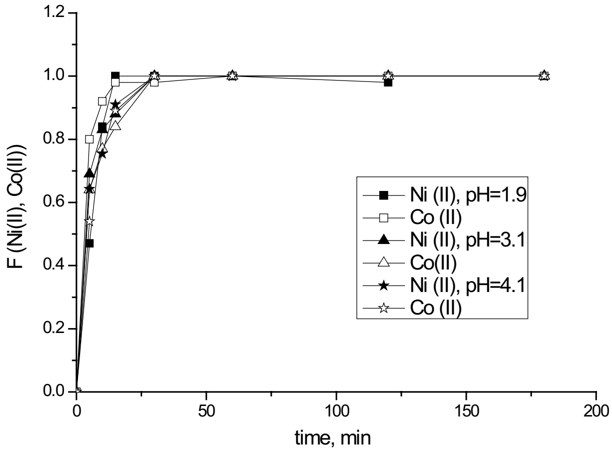

Fig. 1. Effect of pH on the value of *F* for Ni(II) and Co(II) at different extraction times, for a concentration of 0.05 g/L ions, and for a 2-g resin load.

Table 2
Adsorption of Ni(II) and Co(II) by the resin at equilibrium at different pHs

pH	[Ni], mg/g resin	[Co], mg/g resin
1.9	0.61	2.01
3.1	4.46	4.52
4.1	4.95	4.94

Table 3 shows the concentration of Ni(II) and Co(II) onto the resin when the adsorption equilibrium was reached (30 min) at different initial metal concentrations.

3.1.3. Adsorption mechanics

Three adsorption mechanisms were examined to determine which described best the adsorption or ion exchange of Ni(II) and Co(II) ions onto the resin. Tables 4 and 5 show the linear regression coefficients for each of the tested models, employing the *F* values determined above, under the different pH and initial metal concentrations investigated.

Table 4 shows that for metals concentration of 0.05 g/L and a resin weight of 2 g, Ni(II) uptake at pH 1.9 is best described by the film diffusion-controlled mechanism. However, at pH 3.1 and 4.1, the model which best described the metal uptake is the particle diffusion-controlled mechanism. Table 4 also shows that both at pH 1.9 and 3.1, Co(II) adsorption is best described by the particle diffusion-controlled mechanism, whereas at pH 4.1, the metal adsorption is best described by the film diffusion-controlled mechanism.

Table 5 shows that at pH 3.1 and a resin weight of 2 g, the model that best describes the adsorption of Ni(II) differs depending on the initial metal concentration: at 0.05 g/L is the particle-diffusion controlled mechanism, and at 0.1 g/L is

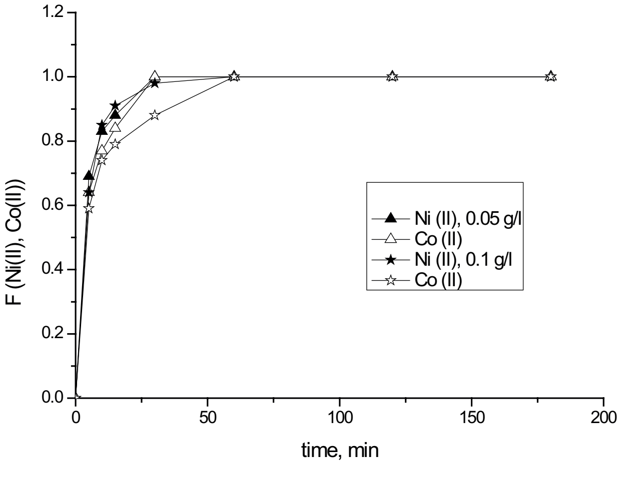

Fig. 2. Effect of the initial Ni(II) and Co(II) concentration (0.05 and 0.1 g/L) on the value of *F* at different extraction times, at a pH of 3.1 and for a 2-g resin load.

Table 3
Adsorption of Ni(II) and Co(II) by the resin at equilibrium for different initial ion concentrations

$[Ni]_0$, $[Co]_0$, g/L	[Ni], mg/g resin	[Co], mg/g resin
0.05	4.46	4.52
0.1	5.99	6.90

the film diffusion-controlled mechanism. The adsorption of Co(II) was described best by the particle-diffusion controlled mechanism for every concentration.

Tables 4 and 5 also show the estimated *k* values for the models and the various experimental conditions.

3.1.4. Kinetic and diffusion coefficients

Using the *k* values showed in Tables 4 and 5, Tables 6 and 7 show the diffusion coefficients at various initial pH values and initial metal concentrations in the aqueous solution, respectively.

In the case of Ni(II), when the pH increased from 3.1 to 4.1 and when the metal concentration is 0.05 g/L, the diffusion coefficient decreased from 4.9×10^{-7} to 3.5×10^{-7} cm²/s. For Co(II), when the pH increased from 1.9 to 3.1 and when the cobalt concentration was constant at 0.05 g/L, the diffusion coefficient decreased from 8.9×10^{-7} to 3.4×10^{-7} cm²/s.

For Ni(II), when the initial ion concentration in the aqueous solution increased from 0.05 to 0.1 g/L at pH of 3.1, the diffusion coefficient decreased from 4.9×10^{-7} to 1.2×10^{-8} cm²/s. For Co(II), when the initial ion concentration in the aqueous solution increased from 0.05 to 0.1 g/L at pH of 3.1, the diffusion coefficient decreased from 3.4×10^{-7} to

Table 4
Linear regression coefficients for each of the tested models – employing the determined *F* values – under different conditions of pH

pH	Coefficients	Ni(II)			Co(II)		
Models		FD-C	PD-C	MBP	FD-C	PD-C	MBP
1.9	R^2	0.985[a]	0.940	0.951	0.995	0.996[a]	0.990
	k, min^{-1}	0.183	0.122	0.043	0.250	0.210	0.054
3.1	R^2	0.983	0.998[a]	0.995	0.968	0.993[a]	0.988
	k, min^{-1}	0.177	0.117	0.042	0.119	0.081	0.028
4.1	R^2	0.966	0.989[a]	0.986	0.999[a]	0.992	0.996
	k, min^{-1}	0.140	0.084	0.031	0.147	0.107	0.036

[a] Model to which results fitted best.
Note: FD-C = film diffusion-controlled process; PD-C = particle diffusion-controlled process; MBP = moving boundary process; R^2 = linear egression coefficient; and *k* = kinetic coefficient (rate constant).
By way of illustration, the results shown for these differing pHs are those obtained at an ion concentration of 0.05 g/L and with a resin load of 2 g.

Table 5
Linear regression coefficients for each of the tested models – employing the determined *F* values – for different initial ion concentrations at a pH of 3.1

Initial ion concentration (g/L)	Coefficients	Ni(II)			Co(II)		
Models		FD-C	PD-C	MBP	FD-C	PD-C	MBP
0.05	R^2	0.983	0.998[a]	0.995	0.968	0.993[a]	0.988
	k, min^{-1}	0.177	0.117	0.042	0.119	0.081	0.028
0.1	R^2	0.999[a]	0.995	0.998	0.958	0.986[a]	0.982
	k, min^{-1}	0.189	0.128	0.045	0.103	0.066	0.024

[a] Model to which results fitted best.
Note: FD-C = film diffusion-controlled process; PD-C = particle diffusion-controlled process; MBP = moving boundary process; R^2 = linear egression coefficient; and *k* = kinetic coefficient (rate constant).
By way of illustration, the results shown for these differing ion concentrations are those obtained at pH 3.1 and with a resin load of 2 g.

Table 6
Kinetic and diffusion coefficients for the adsorption of Ni(II) and Co(II) at different pHs, an initial ion concentration of 0.05 g/L of Ni and a resin load of 2 g

pH		1.9	3.1	4.1
Ni(II)	*k* (min^{-1})	0.183 (3.1×10^{-3} s^{-1})	0.117 (1.9×10^{-3} s^{-1})	0.084 (1.4×10^{-3} s^{-1})
	D (cm²/s)	4.0×10^{-9}	4.9×10^{-7}	3.5×10^{-7}
	t_{50} (s)	420	180	180
Co(II)	*k* (min^{-1})	0.210 (3.5×10^{-3} s^{-1})	0.081 (1.4×10^{-3} s^{-1})	0.147 (2.4×10^{-3} s^{-1})
	D (cm²/s)	8.9×10^{-7}	3.4×10^{-7}	2.2×10^{-8}
	t_{50} (s)	420	180	180

Note: *k* = kinetic coefficient (rate constant); *D* = diffusion coefficient; and t_{50} time at which 50% adsorption equilibrium is achieved.

2.8×10^{-7} cm^2/s. The above values resembled well other data described elsewhere [15].

3.1.5. Batch experiments: Ni(II) and Co(II) desorption

Using an acidic eluant, as HCl solutions, the reactions for Ni(II) and Co(II) desorption from the resin can be described by the following equations:

$$R_2^-Ni^{2+} + 2H^+_{aq} \rightarrow Ni^{2+}_{aq} + 2R - H^+ \tag{10}$$

$$R_2^-Co^{2+} + 2H^+_{aq} \rightarrow Co^{2+}_{aq} + 2R - H^+ \tag{11}$$

moreover, and due to the affinity of chloride ions with cobalt (II) to form anionic complexes, reaction (11) must be rewritten as:

$$R_2^-Co^{2+} + 2H^+_{aq} + 4Cl^-_{aq} \rightarrow CoCl^{2-}_{4_{aq}} + 2R - H^+ \tag{12}$$

Table 7
Kinetic and diffusion coefficients for the adsorption of Ni(II) and Co(II) at different initial ion concentrations, at pH 3.1 and for a resin load of 2 g

Initial ion concentration		0.05 (g/L)	0.1 (g/L)
Ni(II)	k (min^{-1})	0.117 (1.9×10^{-3} s^{-1})	0.189 (3.1×10^{-3} s^{-1})
	D (cm^2/s)	4.9×10^{-7}	1.2×10^{-8}
	t_{50} (s)	180	180
Co(II)	k (min^{-1})	0.081 (1.3×10^{-3} s^{-1})	0.066 (1.1×10^{-3} s^{-1})
	D (cm^2/s)	3.4×10^{-7}	2.8×10^{-7}
	t_{50} (s)	180	180

Note: k = kinetic coefficient (rate constant); D = diffusion coefficient; and t_{50} time at which 50% adsorption equilibrium is achieved.

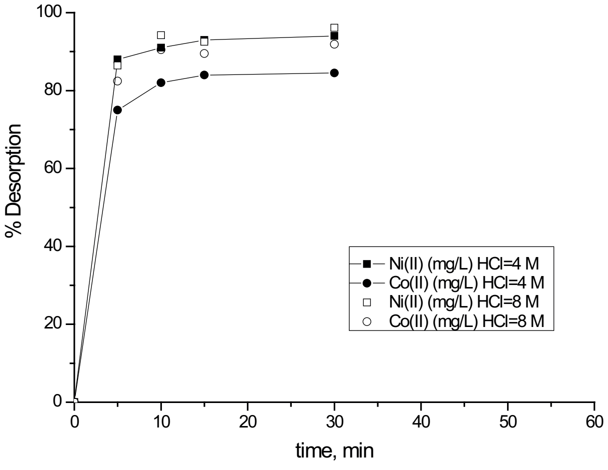

Fig. 3. Desorption of Ni(II) and Co(II) from the resin (load 1 g) by HCl at different concentrations (4 and 8 M; volume of 20 mL).

Fig. 3 shows the results of the batch experiments in which Ni(II) and Co(II) were desorbed from the resin by HCl at different concentrations (4 and 8 M) and at a volume of eluant of 20 mL (experiments performed with 10 mL solutions produced very similar results [data not shown]).

The results show that 5 min of contact is sufficient to allow the recovery of 75% of both ions.

3.2. Continuous experiments: Ni(II) and Co(II) adsorption

The effect of various flow rates on Ni(II) and Co(II) adsorption had been investigated, and the results are shown in Fig. 4. It can be seen that metals uptake increased as the flow rate decreased, whereas cobalt is always adsorbed onto the resin in a lesser extent than nickel.

With respect to the influence of the amount of resin loaded in the column on metals uptake, Fig. 5 allowed to conclude that in both cases, nickel and cobalt, the metal uptake increases as the amount of resin in the column increases, and as described above, cobalt is always loaded onto the resin in a lesser extent than nickel.

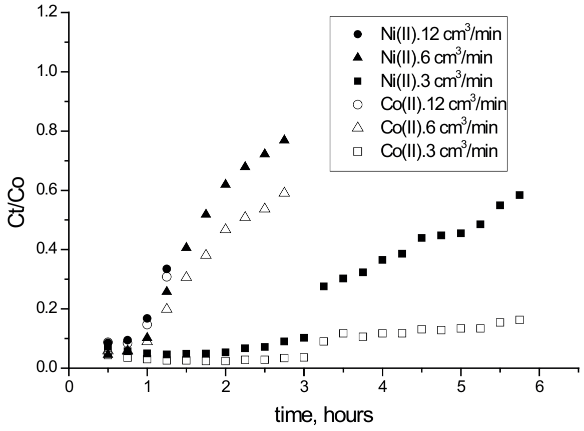

Fig. 4. Effect of flow rate on Ni(II) and Co(II) adsorption over time (initial ion concentration 0.01 g/L, pH = 3.1, resin load 2 g).

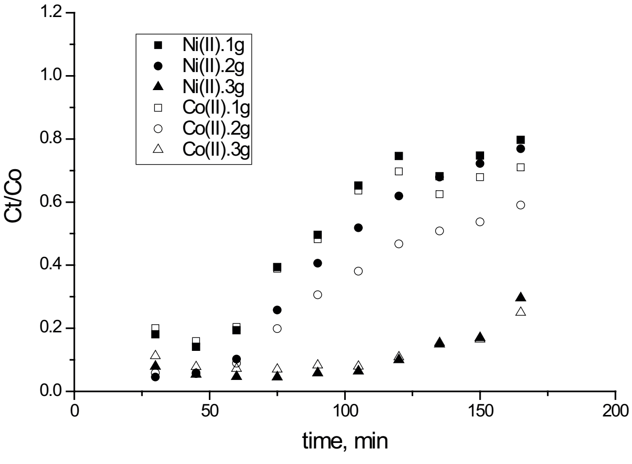

Fig. 5. Effect of resin load on Ni(II) and Co(II) adsorption (initial ion concentration 0.01 g/L, pH = 3.1, flow rate 6 cm^3/min).

4. Conclusions

For both metals, and under all conditions tested, the adsorption or ion exchange equilibrium was reached at about 30 min. The mechanism governing the adsorption of the nickel and cobalt onto Lewatit TP-260 resin may vary between the film diffusion-controlled and particle diffusion-controlled process, depending on the conditions of pH and initial ion concentration. The estimated values of the diffusion coefficients for both ions change with respect to their initial concentrations and pH. Elution experiments showed that 5 min of contact time were sufficient to allow the recovery of around 75% of both, nickel and cobalt, from the metal-loaded resin when either 4 or 8 M HCl solutions were used as eluant. In continuous experiments, metals adsorption improved with decreasing flow rate of the inlet solution and increasing the resin load in the column. Lewatit TP-260 resin could be successfully used in practice to remove Ni(II) and Co(II) from acidic aqueous solutions, although the optimum conditions required need to be yet optimized.

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