Evaluation of chelating ion-exchange resins for separating Cr(III) from industrial effluents

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ABSTRACT

In this study two chelating resins containing iminodiacetic acid groups (Amberlite IRC 748 and Diaion CR 11) and a chelating resin based on sulfonic and diphosphonic acid groups (Diphonix) were investigated in order to separate Cr(III) from industrial effluents produced in hard and decorative electroplating. Samples of two industrial plants were characterized during a period of about one year and a half in terms of the metals content (Cr, Cu, Na, Ca, Fe and Ni), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD) and pH. Some of the physical properties of the resins, namely the moisture content, apparent density, intraparticle porosity and the particle size distribution were also evaluated. To quantify the sorption capacity of the resins, batch experiments were performed using synthetic solutions of Cr(III), as well as solutions of Fe in the case of Diphonix. The Langmuir and Langmuir–Freundlich isotherms enabled a good description of the ion-exchange equilibrium data, and the maximum sorption capacity determined for Amberlite and Diaion was 3.6 mequiv./$g_{dry\ resin}$. For Diphonix that parameter was 3.4 mequiv./$g_{dry\ resin}$. The Diphonix resin exhibits a high selectivity for transition metals (Fe, Ni) over the chromium trivalent. Therefore, it was screened as the most suitable for selectively removing those metal impurities from chromium electroplating effluents. For this resin, the sorption capacity is strongly dependent on the initial pH of the solution. Though, high regeneration efficiencies of Diphonix for stripping Cr(III) were found by using a mixture of NaOH/H_2O_2.

The mathematical model tested for describing the dynamics of the process allowed a good fitting to the experimental data and enabled the estimation of effective pore diffusivity of Cr(III). The saturations of Diphonix with industrial effluents demonstrated that the breakthrough capacity of the resin is affected by the presence of other species in solution, such as Fe and Ni. Nevertheless, these effluents may be treated with this resin, being possible to separate Cr(III) from other transition metallic ions in solution.

1. Introduction

Chromium is an important constituent of industrial effluents generated by metal-finishing industries including the electroplating. According to studies performed by INETI (Engineering and Industrial Technology National Institute), in the year 2000, the Portuguese electroplating industries generated approximately 750 m³ of liquid and 370 tonnes of solid waste containing chromium. The traditional treatments used for metal control in wastewaters are based on pH adjustments for precipitation, flocculation, and sedimentation/filtration. Depending on the metals contained in the effluent, the optimum pH for precipitation is usually in the range of 8.5–11. The main disadvantage of these processes is the production of solid residues (sludges) with toxic compounds, whose final disposal is usually landfilling. Therefore, the use of alternative processes, such as adsorption [1–3], ion-exchange [4–13], membrane [14,15] and biological [16,17] processes is advisable, in order to protect the environment, as well as for recovering at least one valuable metal.

In the last decades, the ion-exchange technology has found widespread application in the removal of heavy metals from industrial wastewaters. The chelating resins are commonly employed as ion-exchange materials, once their ligands can selectively bind to certain metallic ions. Recent studies [8,13,18,19] have shown that these resins could be used for the selective removal and recovery of Cr(III). Kabay et al. [13] evaluated chelating resins containing phosphinic, phosphonic and methylenephosphinic groups for the removal of Cr(III) against pH change, being observed that almost 100% of removal occurred at pH 2–2.5. The same authors [13] used the Diphonix resin for the removal of Cd(II) and Cr(III) from phosphoric acid solutions through column tests. They found that the acid concentration strongly determine the resin behaviour with respect

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Nomenclature

C	solute concentration in the fluid phase, mg/L
d_p	particle diameter, cm
D_{ax}	axial dispersion coefficient, cm^2/s
D_{pef}	effective intraparticular diffusion coefficient, cm^2/s
F	dimensionless concentration in the bulk fluid phase $(=C/C_0)$
H	moisture content (%)
K_L	isotherm parameter
L	bed height, cm
n	isotherm parameter
N_p	number of transfer units by pore diffusion $(= 15(1 - \varepsilon)D_{pef}\tau/(\varepsilon R_0^2))$
Pe	axial Peclet number $(=u_o L/\varepsilon D_{ax})$
q	adsorbed solute concentration in equilibrium with the liquid concentration, mg/g$_{res}$
$\bar{q}$	average adsorbed solute concentration, mg/g$_{res}$
q_m	maximum adsorption capacity of the adsorbent, mg/g
Re	Reynolds number $(=u_o \rho\, d_p/\varepsilon\, \mu)$
R_0	particle radius, cm
t	time, s
T	dimensionless throughput parameter $(=1/\xi(t/\tau - 1))$
T_{Bp}	breakthrough time, s
u_o	bed superficial velocity, cm/s
$\bar{y}$	dimensionless average adsorbed phase $(=t/(\xi\tau)-1)$ concentration, $(= \bar{q}/q_e)$

Greek letters

ε	bed porosity
ε_p	wet particle porosity $(=1 - (\rho_{ap}/\rho_r))$
ξ	capacity factor $(=(1-\varepsilon)\rho_w\, q_e 10^3/(\varepsilon\, Co))$
μ	dynamic viscosity, g/cm s
ρ	density, g/cm^3
ρ_r	real density, g/cm^3
ρ_w	wet density, g/cm^3
ρ_{ap}	apparent density, g/cm^3 $(=\rho_w (1 - H/100))$
τ	space time, s $(=\varepsilon L/u_0)$

Subscripts

e	equilibrium
F	Freundlich
L	Langmuir
LF	Langmuir–Freundlich
Bp	break point
0	feed condition

Table 1
Functional groups and matrix of the resins tested.

Resin	Functional group	Matrix
Amberlite IRC 748	Iminodiacetic acid	Macroporous styrene divinylbenzene
Diaion CR 11	Iminodiacetic acid	Polystyrene
Diphonix	Diphosphonic and sulfonic acid	Polystyrene/divinylbenzene

eluted than the impurities (Fe and Ni). In this context, the objective of the paper is focused on the evaluation of the performance of three different chelating resins, in the sodium form, for uptaking Cr(III). Equilibrium and dynamic behaviour of the process in column, using synthetic and industrial effluents, were investigated. Moreover, the regeneration efficiencies of pre-saturated resins were also determined.

2. Materials and methods

The results of this work were obtained using the materials and experimental procedures described in the next sections.

2.1. Resins and reagents

Chelating resins Amberlite IRC 748 (Rohm & Haas), Diaion CR 11 (Mitsubishi Chemical Corporation) and Diphonix (EIChrom) were used in this study, and their chemical characteristics are shown in Table 1. All the chemicals used were of analytical grade and obtained from Ridel-de-Haën.

2.2. Characterization of the industrial effluents

In this study, two different industrial effluents from hard and decorative chromium electroplating were considered, and both plants are located in Portugal. In these processes the effluents are treated through batch mode. In fact, the liquid samples of untreated effluent were collected in storage tanks that feed the treatment system based on chemical precipitation. Effluent samples collected in hard electroplating plant will be further referred as M1–M9, and in decorative electroplating plant as C1–C8. The sampling was conducted during 16 months and the samples were analyzed immediately, mainly concerning pH and Chemical Oxygen Demand (COD). The concentrations of Cr, Cu, Na, Ca and Fe were quantified by Flame Atomic Absorption Spectrophotometry (FAAS), PerkinElmer 3300. The Total Suspended Solids (TSS) and the Total Dissolved Solids (TDS) were determined as the amount of solids held on a filter with a pore size of 0.45 μm and by evaporating a certain volume of effluent at 105 °C, respectively. The COD was measured by using kits of CSB 1500/COD 1500 from WTW. The pH measurement was carried out using a WTW pH meter—Inolab level 2.

2.3. Physical characterization of the resins

Moisture content, H, was determined by gravimetry after drying the resins at 80 °C. Real density, ρ_r, and wet density, ρ_w, of dry and wet resin, respectively, were evaluated by the displacement of n-heptane in a picnometer. The apparent density, ρ_{ap}, was obtained from the wet density $\rho_{ap} = (1 - H/100)$. The wet particle porosity, ε_p, was calculated considering the real and apparent densities: $\varepsilon_p = 1 - \rho_{ap}/\rho_r$.

The particle size distributions of wet resins were determined in aqueous dispersions by laser diffraction spectroscopy (LDS) technique using Malvern Instrument Mastersize 2000.

to the sorption/elution of cadmium and chromium. Gode and Pehlivan [8] investigated the performance of chelating ion-exchange resins containing iminodiacetic groups for sorption of Cr(III) as a function of concentration, temperature and pH. In this case, the maximum sorption was observed at pH 4.5. Although a large number of studies have been done on the application of chelating and cationic resins for treating synthetic effluents with metals, little works have enabled the assessment of the resins for separating metals from industrial effluent. In this paper, the main motivation is to provide a suitable and economical utilization of chromium from electroplating effluents containing impurities such as iron and nickel. Therefore, the strategy to be adopted consists of the separation of a purified solution containing Cr(III) throughout the saturation step in which the impurities are selectively removed. Moreover, during the first period of the regeneration process the recovery of chromium is still possible once this species is faster

Table 2
Experimental feed conditions for fixed-bed tests.

Run	C_{Cr} (mg/L)	C_{Fe} (mg/L)	C_{Ni} (mg/L)	pH
1[a]	550	–	–	3.2
2[a]	550	–	–	2.0
3[b]	603	29	–	3.4
4[c]	104	3	14	1.4

[a] Synthetic effluent.
[b] Industrial effluent from hard electroplating (sample M9 diluted 1:10).
[c] Industrial effluent from decorative electroplating (sample C8).

2.4. Conditioning of the resins

Before the experiments, the resins were eluted with 2 M HCl and 2 M NaOH solutions (in the case of Diaion CR 11) or 1 M NaCl solution (in the case of Amberlite IRC 748 and Diphonix). This pre-treatment was used to remove solvents and other preparation chemicals. In the case of Diaion, the last step of the conditioning consisted in percolating a solution of NaOH through the column in order to convert the resin to Na^+ form. The excess of OH^- or Cl^- ions was removed from the resins by rinsing with deionized water until the pH of the eluent was 6–7. All the resins were converted into sodium form.

2.5. Equilibrium experiments

The synthetic solutions of chromium and iron were prepared by dissolving appropriate amounts of $Cr(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in deionized water. The sorption of chromium and iron on the resins was studied in batch mode, where 40 mL of a synthetic solution at different initial concentrations were added into a flask with 1 g of pre-conditioned resin. For studying the effect of initial pH of the solution, this variable was adjusted to the desired value by drop wise 0.1 M HNO_3. Regeneration tests of pre-saturated resin (Diphonix) were conducted with different solutions, and 0.5 g of saturated resin with Cr(III) was poured into flasks in contact with 80 mL of different regeneration agents. In the first trials, several acid solutions (HCl, HNO_3, H_2SO_4 and H_3PO_4) were tested at two concentration levels (1 M and 2 M). A mixture of 1 M NaOH and 0.33 M H_2O_2 was also used. The flasks were sealed and kept at constant temperature (25 °C) in a shaker for 24 h. The resins were separated by vacuum filtration using a Buchner funnel and a filter with a porosity of 0.45 μm. Some aliquots of liquid were analyzed in order to determine the concentration of metals and pH of the solution.

2.6. Column experiments

For the column experiments, a glass tube of 1.6 cm internal diameter and 20 cm height, packed with approximately 8–9 g of Diphonix resin was used. These conditions correspond to 7–9 cm of column length and porosity nearly 0.4. The synthetic solution containing Cr(III) ions, as well as the industrial effluent samples were percolated through the column by using a peristaltic pump. A feed flow rate of 5 mL/min was kept constant along all the experiments. Several aliquots were collected at the outlet column and the concentrations of chromium along the time were analyzed as described above. The experimental feed conditions for four runs (run 1 to run 4) are indicated in Table 2, in what respect to Cr, Fe and Ni concentrations and pH.

3. Theory

Continuous fixed-bed columns are commonly used for the removal of heavy metals from aqueous solutions. The analy-

sis of breakthrough curves obtained for describing the dynamic behaviour of the solute concentration, at column outlet, is a key issue in the design of adsorption and ion-exchange columns. Several mathematical models are reported in the literature to represent the dynamics of these processes which should incorporate the equilibrium model that better fits the laboratory data obtained in batch experiments.

3.1. Equilibrium isotherms

The resins used have the functional groups converted to sodium form, and due to the shape of the isotherms obtained it is believed that the ion-exchange process between Na^+ and Cr(III) ions takes place as an irreversible chemical reaction. Thus, the equilibrium ion-exchange between the solid and liquid phases can be modelled by using common adsorption isotherms as follows:

$$\text{Langmuir model} \quad q = \frac{q_{mL}K_L C}{1 + K_L C} \tag{1}$$

$$\text{Freundlich model} \quad q = K_F C^{n_F} \tag{2}$$

$$\text{Langmuir–Freundlich model} \quad q = \frac{q_{mLF}K_{LF} C^{n_{LF}}}{1 + K_{LF} C^{n_{LF}}} \tag{3}$$

where q is the amount of Cr(III) adsorbed in the resin (mg/g_{res}), C is the equilibrium concentration (mg/L), q_{mL} and K_L are the Langmuir parameters, K_F and n_F the Freundlich parameters and q_{mLF}, K_{LF} and n_{LF} the Langmuir–Freundlich parameters.

3.2. Mathematical modelling of monocomponent breakthrough curves

Some authors have reported works directed to the study of breakthrough behaviour, when the adsorption equilibrium is described by irreversible isotherms. More recently, Rodrigues et al. [20] developed a mathematical model that takes into account axial dispersion and pore diffusion, and the equations were derived from the solute material balances inside the particles and in a bed volume element:

$$\frac{\tau(1 + \xi)^2}{\xi Pe} \frac{dF}{dT} + F - \bar{y} = 0 \tag{4}$$

$$\frac{d\bar{y}}{dT} - \frac{N_p}{5} \frac{F}{(1 - \bar{y})^{-1/3} - 1} = 0 \tag{5}$$

where $F = C/C_0$ and $\bar{y} = \bar{q}/q_e$ are the dimensionless concentrations, being C_0 the feed concentration and q_e the solute concentration in equilibrium with C_0; $\tau = \varepsilon L/u_o$ is the space time; T is the throughput variable defined as,

$$T = 1/\xi(t/\tau - 1)) \tag{6}$$

Additional information about the symbols used in the model equations can be found in the Nomenclature section. The model parameters are: the column capacity factor, ξ, the axial Peclet number, Pe, and the number of transfer units by pore diffusion, N_p, defined in the following equations:

$$\xi = \frac{(1 - \varepsilon)}{\varepsilon} \frac{\rho_w \times 10^3 q_e}{C_0} \tag{7}$$

$$P_e = \frac{u_o L}{\varepsilon D_{ax}} \tag{8}$$

$$N_p = \frac{1 - \varepsilon}{\varepsilon} \frac{15}{R_0^2} D_{pef} \tau \tag{9}$$

Table 3
Physical and chemical characterization of different industrial effluent samples.

Sample	Cr (mg/L)	Cu (mg/L)	Na (mg/L)	Ca (mg/L)	Fe (mg/L)	TSS (mg/L)	TDS (mg/L)	COD (mg/L)	pH
Effluent from hard chromium electroplating process
M1	729.0	5.9	56.0	68.9	15.6	<10	(a)	<100	2.6
M2	683.7	3.3	1897	70.9	17.8	207	7760	<100	2.3
M3	723.9	5.1	73.3	108	20.0	21.7	2250	130	2.6
M4	582.0	2.4	53.9	115	16.8	55.0	1770	260	2.9
M5	1170	5.6	115	1102	28.9	52.7	3340	160	1.9
M6	989.2	4.3	389	61.3	20.5	113	2740	210	4.7
M7	8049	48	151	312	375	401	1960	1030	1.4
M8	1099	7.8	893	698	38.9	103	6800	1050	2.3
M9	6030	44	91.0	3.83	290	100	1470	440	1.6

Sample	Cr (mg/L)	Cu (mg/L)	Na (mg/L)	Ca (mg/L)	Ni (mg/L)	TSS (mg/L)	TDS (mg/L)	COD (mg/L)	pH
Effluent from decorative chromium electroplating process
C1	2294	7.75	42.6	23.9	27.6	<10	(a)	<100	1.6
C2	5958	20.7	39.1	21.0	92.9	<10	14000	<100	1.8
C3	54.17	1.69	12.7	35.2	21.7	13.3	320	<100	5.0
C4	850.7	2.42	14.8	25.0	18.3	<10	2200	<100	2.4
C5	328.8	3.52	6.43	44.3	15.6	<10	970	<100	3.0
C6	603.5	3.13	10.9	38.9	15.0	<10	1500	<100	2.3
C7	12992	27.7	40.9	10.8	84.6	<10	24300	220	1.1
C8	103.5	1.69	12.3	35.2	14.2	<10	780	<100	1.3

(a): not determined.

The axial dispersion was evaluated using the Butt correlation [21]:

$$\frac{u_o d_p}{D_{ax}} = 0.2 + 0.011 Re^{0.48} \qquad (10)$$

where Re is the Reynolds number.

Eqs. (4) and (5) were numerically integrated with the DLSODE package using the initial conditions,

$$T \leq T_{Bp}, \quad F = \bar{y} = 0 \qquad (11)$$

where T_{Bp} was evaluated from the breakthrough time, which corresponds to the break point.

4. Results and discussion

The main objective of this work was to assess the performance of chelating resins for separating Cr(III) from electroplating effluents. To achieve this goal, three resins and several samples of two different industrial effluents were characterized. Moreover, the ion-exchange process was evaluated by determining the equilibrium isotherms. The regeneration efficiency and the dynamic behaviour of the saturations in column were analyzed for the resin selected.

### 4.1. Characterization of industrial effluents

The characterization of both industrial effluents involved the analysis of several parameters and the results are shown in Table 3. The most important issue for both effluents deals with the variability of the chromium concentration. Indeed, for samples from hard electroplating (M1–M9) the concentration was in the range of 582–8049 mg/L. For decorative electroplating (C1–C8) the concentration varied between 55 mg/L and 3000 mg/L. Besides chromium, also other transition metals (Fe, Ni and Cu) were detected in lower quantities. Some samples exhibit high concentrations of Na and Ca, which may interfere in the ion-exchange process. Regarding the TSS, low quantities were observed. In opposite, the TDS can achieve high values, which are undesirable for the process. The COD must also be taken into account, since high values of organic material (M7 and M8) may require a pre-treatment of the effluent before contacting the resin. The pH of the samples was between 1 and 5, and in general it was found that lower pH values correspond to samples with higher chromium concentration.

Table 4
Characteristic parameters of the ion-exchange resins.

Property	Amberlite IRC 748	Diaion CR 11	Diphonix
Moisture content (%)	62.7	60.9	58.3
Apparent density (g dry resin/cm^3 resin)	0.35	0.46	0.40
Wet particle porosity	0.74	0.68	0.70

4.2. Characterization of the resins

Some physical characteristics of used resins were determined and are indicated in Table 4. No significant differences with respect to the moisture content, apparent density and particle porosity were detected. The particle size distributions of the resins were based on volume and the results are presented in Fig. 1. From this figure it is noticeable that 50% (d_{50}) of the particles of Amberlite have diameters less than 574 μm, whereas those values for the particles of Diaion and Diphonix are 524 μm and 223 μm, respectively. Indeed, the Diphonix is characterized by smaller particles and all of them are in the range of 100–400 μm. The particle size distributions of the other resins (Amberlite and Diaion) are larger, consisting of
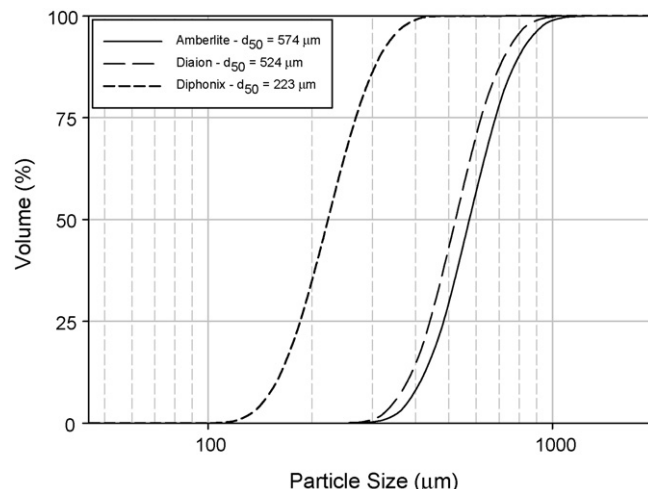
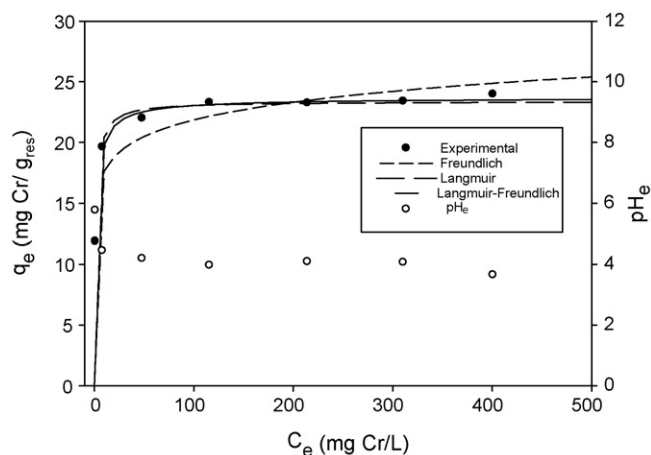**Fig. 1.** Particle size distribution based on volume for the studied resins.

Fig. 2. Ion-exchange equilibrium data for Amberlite: model fitting and pH values.

Fig. 3. Ion-exchange equilibrium data for Diaion: model fitting and pH values.

particles in the range of 300–1000 μm. In the literature, for other commercial resins, such as Lewatit TP 207 and Chelex 100, were indicated bead size ranges of 400–1250 μm and 300–1000 μm, respectively [8]. Also Alguacil and co-workers have referred a range of 450–600 μm for Amberlite IR 120 [23]. It is important to note that the particle size of beads determine the kinetics of the ion-exchange mechanism, having thus a significant effect in the performance of the process in column. As it will be analyzed in Section 4.4, the key parameter of the mathematical model (number of transfer units by pore diffusion, N_p) depends on the particle radius.

4.3. Equilibrium studies

4.3.1. Isotherm parameters evaluation and resin screening

The experimental and calculated data of the ion-exchange equilibrium for the sorption of Cr(III) on the resins tested are depicted in Figs. 2–4. The shape of these curves shows that the resins have a significant affinity to chromium, being the equilibrium isotherm almost irreversible for all the cases. The Diaion and Amberlite resins have nearly the same maximum sorption capacity of 3.6 mequiv./$g_{dry\ resin}$. For Diphonix, the sorption capacity is slightly lower, being equal to 3.4 mequiv./$g_{dry\ resin}$. In the case of Diaion and Amberlite, the minimal values of the capacities claimed by the manufacturers are 1.2 mequiv./$g_{dry\ resin}$ and 1.8 mequiv./$g_{dry\ resin}$, respectively. In the literature, some works also report exchange capacities of resins with similar characteristics to the ones considered in our work, such as the chelating resins Lewatit TP 207 and Chelex 100 whose values are 1.02 mequiv./g and 0.86 mequiv./g [8]. For a macroporous cation exchange resin, the Amberlite IR 120, a capacity value of 3.91 mequiv./g was reported [23].

The equilibrium models indicated previously were fitted to the experimental data and the parameters were calculated by using a
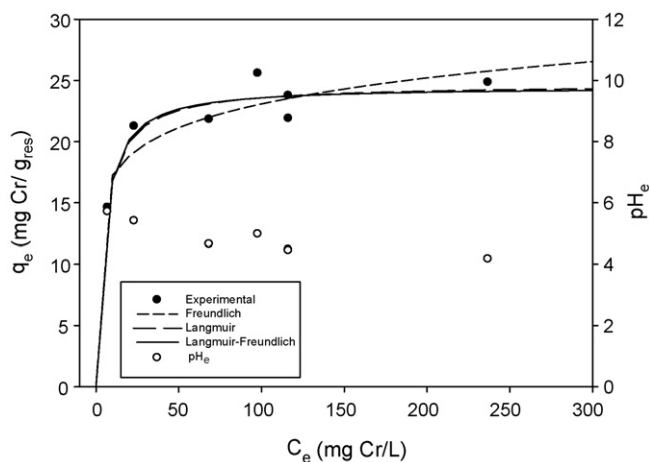

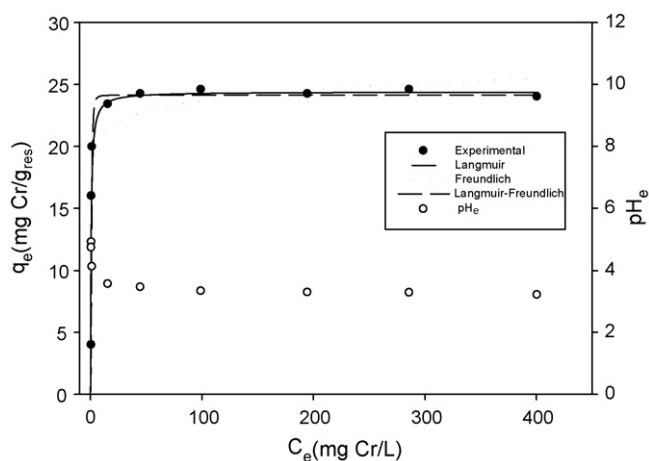**Fig. 4.** Ion-exchange equilibrium data for Diphonix: model fitting and pH values.

non-linear optimization routine (GREG software). The parameters determined for each resin by fitting different equilibrium models are presented in Table 5. According to the sum of the square errors (SS), the best fitting to the experimental data was achieved with the Langmuir–Freundlich model for the three resins. However, for Diaion and Diphonix resins the Langmuir model was considered instead of Langmuir–Freundlich model, since the n_{LF} values do not have physical meaning in this case. The equilibrium pH as function of the chromium concentration is also illustrated in Figs. 2–4, being observable that all the pH values are in the range of 2–6. For Amberlite and Diaion, the sorption of Cr(III) leads to an increase of the solution pH ($\Delta pH = pH_{final} - pH_{initial} > 0$) due to the exchange between Na$^+$ from the resin and H$^+$/Cr(III) in solution. Contrar-

Table 5
Isotherm parameters for sorption of Cr(III) on three different ion-exchange resins.

	Langmuir			Freundlich			Langmuir–Freundlich			
	q_{mL} (mg Cr/g_{res})	K_L (L/mg Cr)	SS	K_F (L/g_{res})	n_F	SS	q_{mLF} (mg Cr/g_{res})	K_{LF} (L/g_{res})	n_{LF}	SS
Amberlite	23.37 3.61[a]	0.69	1.19	14.23	0.093	18.6	23.71 3.67[a]	0.76	0.82	0.62
Diaion	24.70 3.64[a]	0.21	10.1	12.86	0.13	18.1	24.44 3.61[a]	0.17	1.10	10.1
Diphonix	24.40 2.73[a]	1.79	3.22	18.55	0.053	17.9	24.13 2.68[a]	0.99	2.63	0.94

[a] mequiv. Cr/$g_{dry\ resin}$.
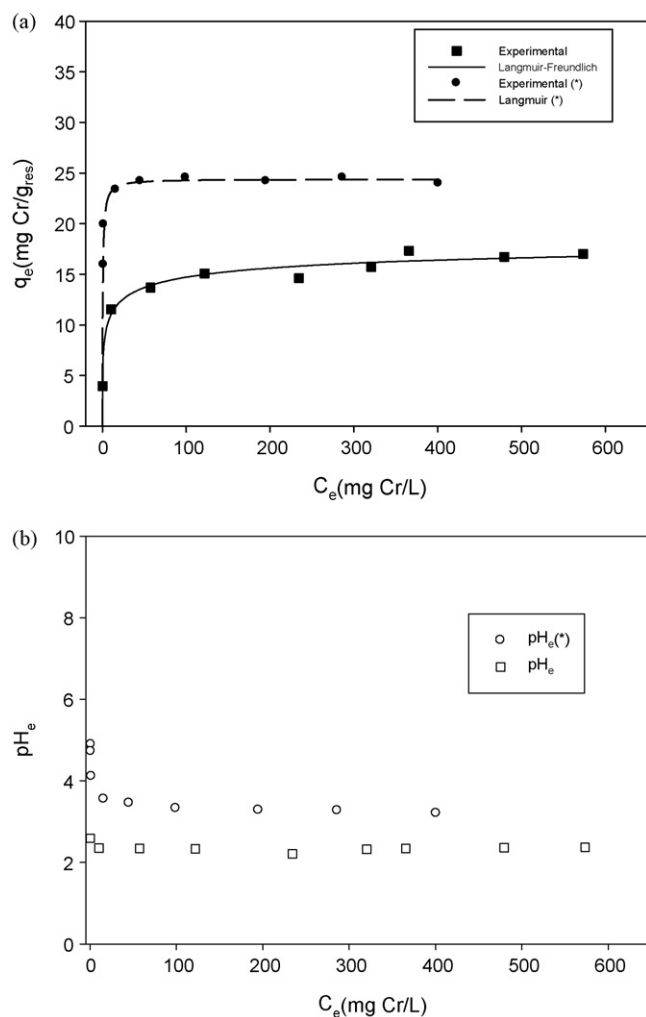
Table 6
Isotherm parameters for Cr(III) and iron sorption on Diphonix resin (at initial pH adjusted to 2).

	Langmuir			Freundlich			Langmuir–Freundlich			
	q_{mL} (mg Cr/g_{res})	K_L (L/mg Cr)	SS	K_F (L/g_{res})	n_F	SS	q_{mLF} (mg Cr/g_{res})	K_{LF} (L/g_{res})	n_{LF}	SS
Cr(III)	16.1 2.22[a]	0.24	18.7	7.42	0.14	8.50	19.83 2.74[a]	0.53	0.37	3.03
Fe(III)	31.9 4.11[a]	1.66	2.62	16.83	0.11	70.2	35.08 4.52[a]	0.97	0.44	28.7

[a] mequiv./$g_{dry\ resin}$.

ily to this behaviour, for Diphonix, the ΔpH values are negative, which may indicate that not all the groups were exchanged by Na$^+$ ions. For all the cases, the ΔpH decreases as initial Cr concentration increases, because the pH$_{initial}$ is lower for the solutions with higher concentrations of chromium.

As referred before, the resins tested exhibit similar capacities for uptaking Cr(III). According to the literature [22,24], for solutions containing trivalent chromium and transition metals such as iron, copper and nickel, the Diphonix has the best selectivity for these metals over Cr(III). In our study, this resin was also screened as the most suitable for treating the electroplating effluents under investigation, enabling the chromium recovery to be further reused in the process. In Fig. 5(a) and (b) two sets of experiments were represented in order to evaluat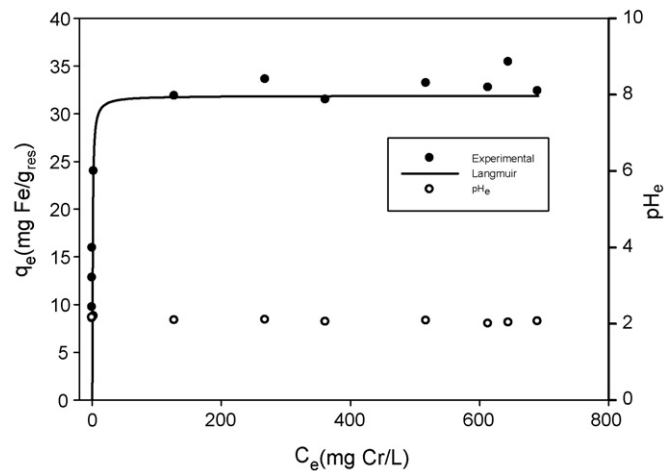e the effect of initial pH of the solution on the Cr(III) adsorbed by the resin. In one case, the initial pH of the solutions was adjusted to 2, and in the other case the initial pH was not controlled, being these results marked with (*) in those figures. The amount of chromium exchanged at lower initial pH was lower than those exchanged at higher pH. This is so because the functional groups of the resin tend to become protonated at low pH solutions. Thus, the metallic ions are less preferred by the resin under these conditions. In the case of pH not adjusted, the initial pH of the solutions of Cr(III) was in the range from 3.2 to 3.8 and the sorption data were well correlated with the Langmuir model as already shown.

Bearing in mind the objective of the work aiming the separation of Cr(III) from electroplating effluents containing metal impurities, iron was considered in the context of the equilibrium studies not only because it is often associated to electroplating effluents, but also due to its positive effect as catalyst during the regeneration process with NaOH/H$_2$O$_2$ solution. Fig. 6 shows the equilibrium data for the sorption of Fe at initial pH adjusted to 2. As shown in Table 6, the Langmuir model was found to be the best fitting isotherm, being the sorption capacity equal to 4.1 mequiv./$g_{dry\ resin}$. By comparing these results with ones obtained for Cr in the same conditions (Table 6), it may be concluded that the Diphonix exhibits greater capacity for iron than for chromium. Therefore, the resin is more selective for Fe and thus this issue should be taken into account in the treatment of industrial effluents.

4.3.2. Regeneration efficiencies for Diphonix resin

The sorption processes are cycling fixed-bed operations in which the regeneration step plays a crucial role in the global performance of the system. For Diphonix resin, different acid solutions and a mixture of NaOH and H$_2$O$_2$ were tested. Fig. 7 shows that low efficiencies (below 60%) to strip Cr(III) were achieved using solutions of strong acids. The efficiency is significantly affected by increasing the acid concentration from 1 M to 2 M for HCl and H$_3$PO$_4$, while the concentration change for other acids has little effect. However,

Fig. 5. Effect of initial pH on ion-exchange for Diphonix/Cr(III): (a) equilibrium isotherms for pH = 2 and pH not controlled (*); (b) equilibrium pH.

Fig. 6. Experimental and calculated ion-exchange equilibrium data for Diphonix/Fe(III) at pH$_{inlet}$ = 2.
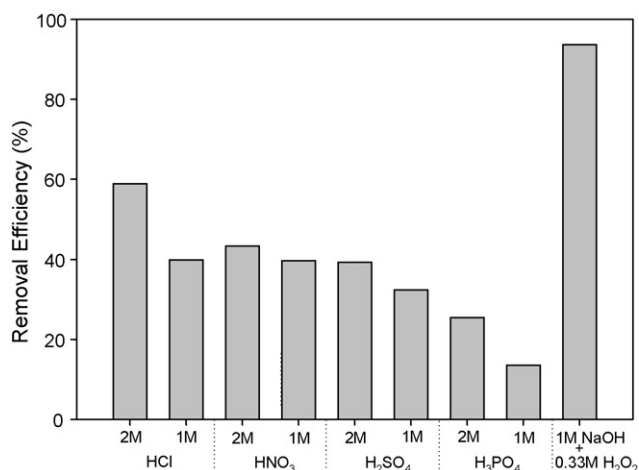
Fig. 7. Regeneration of Diphonix resin with different solutions.

Fig. 9. Breakthrough curves of Cr(III) and Fe (run 3), for sample M9 of hard electroplating process.

it is known that the displacement of Cr(III) from the cation exchangers by using acid regenerants is problematic because of its strong adsorption affinity for the functional groups of the cationic resins. If a prolonged period of contact between the resin and the acid occurs, hydrolyzed and surface-precipitated hydroxo-Cr(III) species are irreversibly adsorbed [12]. The use of $NaOH/H_2O_2$ as regenerant solution enabled to overcome the difficulties of the Cr(III) desorption. This is achieved by the oxidation in alkaline medium of Cr(III) to Cr(VI) in the anionic form CrO_4^{2-} that is rejected by the cationic resin. Indeed, efficiencies of approximately 94% (Fig. 7) were found for experiments of regeneration using the mixture 1 M NaOH and 0.33 M H_2O_2.

4.4. Column tests

Experiments in column were performed to study the dynamic behaviour of the ion-exchange process for separating trivalent chromium from synthetic and industrial effluents. The results are presented as breakthrough curves obtained from complete saturation of the column. As referred previously, the main objective of the work is to recover Cr(III) solution during the saturation step by selectively removing the impurities of the electroplating effluent. The selectivity and the sorption capacity of the resin are two key parameters that should be analyzed to determine the process fea-
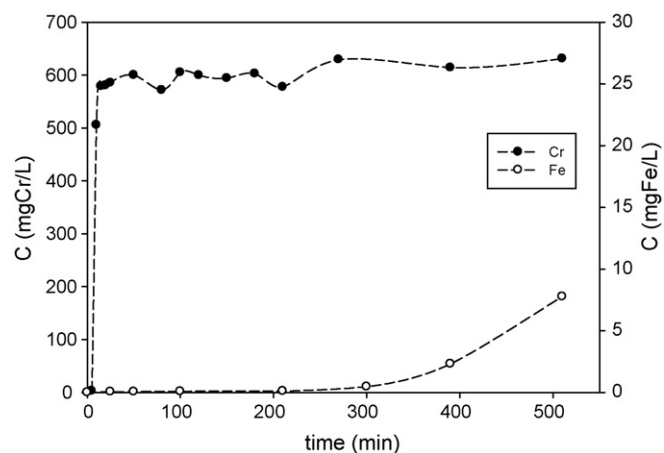
sibility for practical application. The values of these parameters for ionic species depend on flow rate, pH, metal concentration and the existence of other species in solution. Firstly, the study presented in this section is focused on the effect of feed pH on the sorption capacity of Diphonix resin for Cr(III) dissolved in a synthetic solution. Secondly, the study is directed to the evaluation of the resin behaviour in terms of its capacity and selectivity when industrial effluents containing metal impurities (e.g. Fe and Ni) are treated. The breakthrough curves, plotted as metal concentration at column outlet against time, are illustrated in Fig. 8 for synthetic solutions and in Figs. 9 and 10 for the industrial effluents. Fig. 8 shows the effect of pH of the feed solution on the capacity of Diphonix to uptake Cr(III). As demonstrated in the equilibrium studies, also in the column experiment was observed that the adsorption capacity is strongly influenced by the pH of the solution. In fact, the breakthrough time of the saturation curve changed from 42 min to 20 min when the pH of the feed was changed from 3.2 to 2.0. In order to choose the best operating conditions with respect to pH, it is desirable to treat a solution with moderate acidity, pH = 3–4, to favour a high uptake of Cr(III), since this element can be further recovered during the regeneration process. For pH higher than 4–5, metal hydroxide may precipitate inside the resin particles. This effect should be considered in the treatment of industrial effluents. The simulation studies showed a good fitting between experimental and simulated results, being the model solution (Eqs. (4) and (5)) achieved with the following parameter values: $\xi = 78.4$, $Pe = 230$
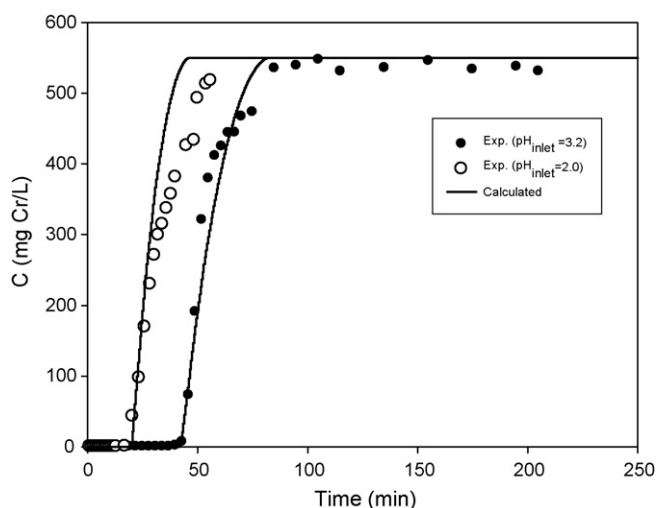

Fig. 8. Experimental and simulated breakthrough curves of Cr(III) for synthetic effluent: (●) run 1 and (○) run 2.
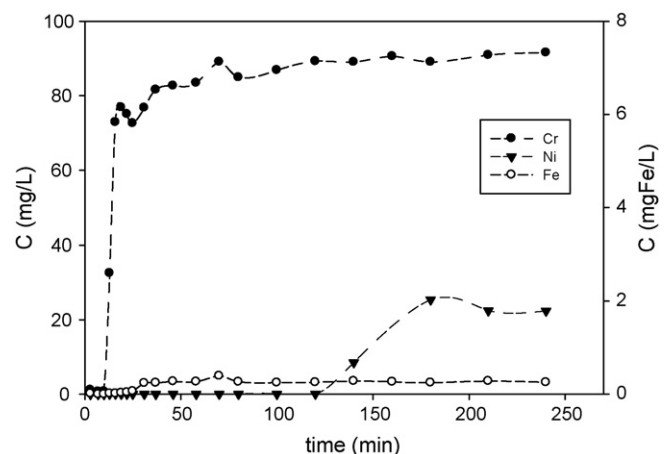

Fig. 10. Breakthrough curves of Cr(III), Ni and Fe (run 4), for sample C8 of decorative electroplating process.

and $N_p = 4.7$ for run 1; $\xi = 51.1$, $Pe = 180$ and $N_p = 3.7$ for run 2. The number of transfer units by pore diffusion, N_p, was the only parameter estimated by fitting the model equations to the experimental breakthrough data, enabling thus the determination of the effective pore diffusivity for Cr(III), $D_{pef} = 5.6 \times 10^{-11}$ cm²/s. The Peclet numbers estimated are high for both runs, and therefore the axial dispersion can be neglected. With respect to the capacity factor, ξ, and according to Eq. (7), its value depends on the capacity of the resin, q_e. Therefore, as initial pH increases the final concentration of Cr(III) adsorbed by the resin, q_e, under saturation conditions of the resin also increases, leading to higher ξ values. The simulation studies showed that the mathematical model used may be a valuable tool for understanding the system under analysis.

Figs. 9 and 10 illustrate the performance of the Diphonix resin for treating industrial effluent samples (M9 and C8), whose properties were indicated in Table 3. Before feeding the column, the sample M9 was diluted 1:10, due to its high concentration in chromium. By analyzing the saturation curves represented in these figures, it may be concluded that the breakthrough capacity of the resin for Cr(III) is affected by the presence of other metals in the effluent, such as iron and nickel. The break point of the saturation curve for the Cr(III) emerges almost immediately and earlier when compared with the curves shown in Fig. 8 (for synthetic effluent). The breakthrough curves of Fe and Ni emerge later since the resin has higher preference for these metals, and also due to lower feed concentrations of these metals when compared with Cr. Thus, the treatment of the industrial effluent with the Diphonix resin makes possible the selective separation of the metallic ions under study. In Figs. 9 and 10, it is evident that a solution of high purity of Cr(III) can be recovered for reuse, during approximately 300 min and 120 min of resin saturation of the resin in runs 3 and 4, respectively.

5. Conclusions

Three chelating ion-exchange resins (Amberlite IRC 748, Diaion CR 11 and Diphonix) in the sodium form were tested for separating Cr(III) from synthetic and industrial effluents. The equilibrium results showed that the all resins have a strong affinity for chromium ions. The ion-exchange isotherms are almost irreversible and well fitted with the Langmuir and Langmuir–Freundlich models. From this analysis, the maximum sorption capacity determined for Amberlite and Diaion was 3.6 mequiv./g$_{dry\ resin}$, and for Diphonix was 3.4 mequiv./g$_{dry\ resin}$. The Diphonix resin was screened as the most suitable for separating Cr(III), since it exhibits high selectivity for transition metals (Fe, Ni) over the chromium trivalent, enabling thus selective removal of those metal impurities from chromium electroplating effluents. The sorption capacity is influenced by the initial pH of the solution, and low pH leads to lower sorptions. From regeneration experiments, it can be concluded that NaOH/H$_2$O$_2$ solutions can be used for stripping Cr(III) from the Diphonix resin.

For synthetic effluent, the behaviour of the breakthrough curves obtained from the saturation of the Diphonix with Cr(III) was significantly affected by the pH of the feed. The mathematical model used for describing the dynamics of the process yields results in good agreement with the experimental data and enabled to estimate the effective pore diffusivity for Cr(III). The saturations of the resin with industrial effluents showed that the breakthrough capacity of the resin is affected by the presence of other ions in solution, such as Fe and Ni. However, the treatment of real effluents with this resin enables to separate Cr(III) from other transition metallic ions and, simultaneously its recovery.

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