

Removal of chromium from electroplating industry effluents by ion exchange resins

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Abstract

Effluent discharged from the chromium electroplating industry contains a large number of metals, including chromium, copper, nickel, zinc, manganese and lead. The ion exchange process is an alternative technique for application in the treatment of industrial wastewater containing heavy metals and indeed it has proven to be very promising in the removal and recovery of valuable species. The main objective of the present work is to evaluate the performance of commercial ion exchange resins for removing chromium trivalent from industrial effluents, and for this purpose two resins were tested: a chelating exchange resin (Diaion CR11) and a weak cationic resin (Amberlite IRC86). In order to evaluate the sorption capacity of the resins some equilibrium experiments were carried out, being the temperature and pH the main variables considered. The chromium solutions employed in the experiments were synthetic solutions and industrial effluents. In addition, a transient test was also performed as an attempt to understand the kinetic behaviour of the process.

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1. Introduction

Metal surface treatment is one of the major metal working processes that generates a large amount of liquid and solid (sludge) wastes containing heavy metals. According to studies performed by the Waste's Institute of the Ministry of Environment, this waste represented about 0.9% of the overall production (25,400 tonnes) of hazard industrial wastes in Portugal during the year 2001. Heavy metals are important sources of environmental pollution, being some of them very toxic even at low concentrations. The traditional techniques used for metal control are based on chemical precipitation coupled to pre- or post-oxidation/reduction followed by filtration in order to concentrate the species of interest. The main disadvantage of these techniques is the production of solid residues (sludges) containing toxic compounds whose final disposal is in general landfilling (which is the last priority in terms of EU policies). Therefore, the use of other alternative techniques (such as adsorption, ion exchange, membrane and biological processes) based on physical, chemical and biological mechanisms is advis-

able in order to protect the environment and at the same time recovering at least a valuable metal. In the case of the chromium (case studied), the chromate form can be recovered from an effluent and reused in the plating industry or in tanneries after reduction to Cr(III). The selection of this heavy metal is based on health concerns, since hexavalent chromium is potentially carcinogenic when inhaled [1–3], as well as due to its commercial value.

Several studies considering the Cr removal by ion exchange resins have been reported in the literature. Petruzelli et al. [4] reported the IERECHROM process based on the use of a macroporous carboxylic resin that allows the removal of almost pure Cr from other interfering metals. Chmielewski et al. [5] implemented a method for recovering Cr, Cu and water from electroplating wastewater using a combined process involving electrochemical oxidation and ion exchange. Lin and Kiang [6] proposed a procedure to recover chromic acid from a waste acid solution using a multi-step ion exchange process, where a large amount of regenerant chemicals were spent. Yalçın et al. [7] developed a laboratory-scale separation process for the recovery of Cr(VI) and Cr(III) with a strongly basic resin and a weakly acidic resin, respectively. Rengaraj et al. [8] performed equilibrium and kinetics experiments to evaluate the sorption capacity of chromium by three different strongly acid resins.

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Some chelating resins show high affinity to chromium, which can be considered an advantage in the wastewater treatment [9–11]. The uptake of chromium by ion exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [12,13]. Ion exchange resins have been also used to remove other metals from electroplating waste waters [14,15].

In the present work the removal of Cr(III) from aqueous solutions using a chelating exchange resin (Diaion CR11) and a weak cationic resin (Amberlite IRC86) was investigated. The main objective of the study was to evaluate the sorption equilibrium for these resins at two different temperatures. Moreover, a preliminary experiment was also performed in order to understand the dynamic behaviour of the process in a column test.

2. Materials and methods

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

2.1. Ion exchange resins and reagents

The chelating resin Diaion CR11 (Mitsubishi Chemical Corporation) and the weak cationic resin Amberlite IRC 86 (Rohm and Haas) were used in this study. In the case of Diaion CR11, the matrix is polystyrenic and the chelating group is the iminodiacetic acid. For Amberlite IRC 86, the functional group is the carboxylic acid and the matrix is a polyacrylic copolymer. All the chemicals used were of analytical grade and were obtained from Ridel-de-Haën.

2.2. Conditioning and regeneration of the resins

Before the experiments, the resins were pretreated by repeated washings with 2 M HCl and 2 M NaOH solutions to remove solvents and other preparation chemicals. The last step of the conditioning consisted in percolating a solution of NaOH or HCl through the column in order to convert the resins to Na⁺ or H⁺ form, respectively. The excess of OH⁻ or Cl⁻ groups were removed from the resins by rinsing with deionized water. Different solutions with strong acids or bases were used for the regeneration of the exhausted resins. A solution of 1 M NaOH and 0.15 M H₂O₂ proved to be reasonably effective for stripping Cr(III) from the resins Amberlite IRC86 and Diaion CR11. For this last, it was necessary to leave the resin in contact with the solution for about 24 h.

2.3. Equilibrium experiments

For these experiments, samples of synthetic effluent were prepared by dissolving an appropriate amount of chromium salt (Cr(NO₃)₃·9H₂O) and copper salt (Cu(NO₃)₂·2.5H₂O) in distilled water. An industrial effluent from a plating metal industry was also utilized.

The sorption of chromium(III) on the resins was studied through batch tests, where 75 ml of a synthetic solution of

chromium nitrate at different initial concentrations of chromium were added into a flask with 2 g of preconditioned resin. The flasks were sealed and placed in a constant temperature shaker at 25 or 50 °C for 24 h (Diaion CR11) or 48 h (Amberlite IRC 86). The resins were separated by filtration and some aliquots of liquid were analysed using flame atomic absorption spectrophotometry in order to determine the total concentration of the metal in solution.

2.4. Column experiments

In the column experiment, a glass tube with 1.6 cm internal diameter and 20 cm height, packed with 9 cm of resin (8.5 g) was used. A peristaltic pump was utilized to percolate 10 ml/min through the column of a synthetic solution containing 732 mg/l of Cr³⁺ and 6.4 mg/l of Cu²⁺. Several samples were collected at the outlet column and the concentrations of chromium and copper along the time were analysed as described above.

3. Results and discussion

Considering that the main objective is the removal of chromium trivalent from electroplating effluents, this study show preliminary results in order to evaluate the performance of two commercial resins. The results comprehend mainly the characterization of the industrial effluent, the determination of equilibrium ion exchange isotherms and the analysis of dynamic behaviour of saturation in column.

3.1. Characterization of the industrial effluent

Two samples of an industrial effluent were collected from a chromium electroplating industry located in the centre region of Portugal, being the Cr and Cu quantified. Other species and parameters were also evaluated using standard analytical methods and the results are shown in Table 1. The sample 1 (S1) and sample 2 (S2) were collected with an elapsed time approximately of 2 months. As expected, the samples are moderately concentrated in chromium, containing also other heavy metals in lower quantities (Cu, Fe, traces of Ni and Zn). The concentrations of Na and K in the sample S2 are much higher than in the sample S1 due to the process industrial conditions. Since the CQO is low, the main pollution problem of this effluent is related with inorganic elements, whose concentration in the samples analysed is rather above of the maximum allowed by the Portuguese legislation: 3.0 and 0.1 mg/l for trivalent and hexavalent forms, respectively.

3.2. Characterization of the resins

Some physico-chemical characteristics of the used resins were determined and indicated in Table 2. The apparent density, ρ_{ap} , was obtained from the real density of the wet resin sample (evaluated by the displacement of *n*-heptane in a pycnometer) and the moisture content. The wet particle porosity, ϵ , was evaluated considering the real and apparent densities.

Table 1
Characteristics of two industrial effluent samples

	Cr (mg/l)	Cu (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	pH	TDS (mg/l)	CQO (mg/l)
S1	729.0	5.9	56.0	2.7	68.9	9.3	15.6	2.6	(a)	<100
S2	683.7	3.3	1897	468	70.9	5.8	17.8	2.3	7763	<100

(a): not determined.

Table 2
Characteristics of the ion exchange resins

Property	Diaion® CR11	Amberlite® IRC 86
Moisture content (%)	61.3	68.0
Apparent density, ρ_{ap} (g dry resin/cm ³ resin)	0.38	0.43
Wet particle porosity, ε	0.73	0.74
Total capacity (mequiv. Na ⁺ /g resin)	1.21	2.77

The ion exchange capacities of the resins in the Na⁺ form were obtained by the potentiometric titration method, and the curves are given in Fig. 1. For Diaion CR11 one equivalence point is detected, and for Amberlite IRC86 two points are observed, meaning that there are two dissociating groups associated to this resin. The results showed in Table 2 indicate that the Amberlite has a total capacity almost twice higher than the Diaion.

3.3. Equilibrium ion exchange isotherm

For describing the adsorption equilibrium, the following model is commonly employed:

$$\text{Langmuir model } q = \frac{q_{\max} K_L C}{1 + K_L C} \quad (1)$$

where q is the amount adsorbed in the resin (mg/g_{wetres}), C is the equilibrium concentration (mg/l) and q_{\max} and K_L are the isotherm parameters.

3.3.1. Diaion CR11

The resin, either in the H⁺ or in the Na⁺ form, was tested at two different temperatures (25 and 50 °C). The experimental

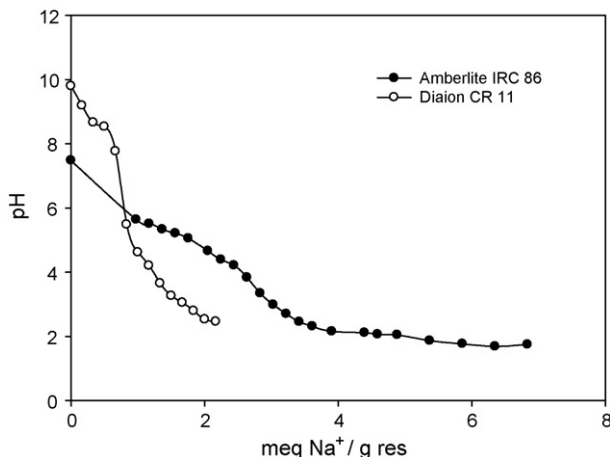


Fig. 1. Potentiometric titration curves for the resins Diaion and Amberlite.

data corresponding to the equilibrium isotherms using synthetic solutions of Cr³⁺ with different concentrations are presented in Fig. 2. The shapes of the curves show that the resin has a significant affinity to the chromium and the sodium form exhibits higher sorption capacity than the resin converted to the hydrogen form.

From Fig. 2, it can also be concluded that the sorption capacity of chromium increases with the temperature, being this fact more evident in Fig. 2(a). Even though in Fig. 2(b) this difference is not so large, it can be confirmed by comparing the maximum capacities (q_{\max}) at 25 and 50 °C for the resin in the Na⁺ form. The sorption capacity of conventional resins generally decreases when the temperature increases. However, in the case of chelating resins the opposite effect can occur depending on how the equilibrium constant of the chelate complex formed

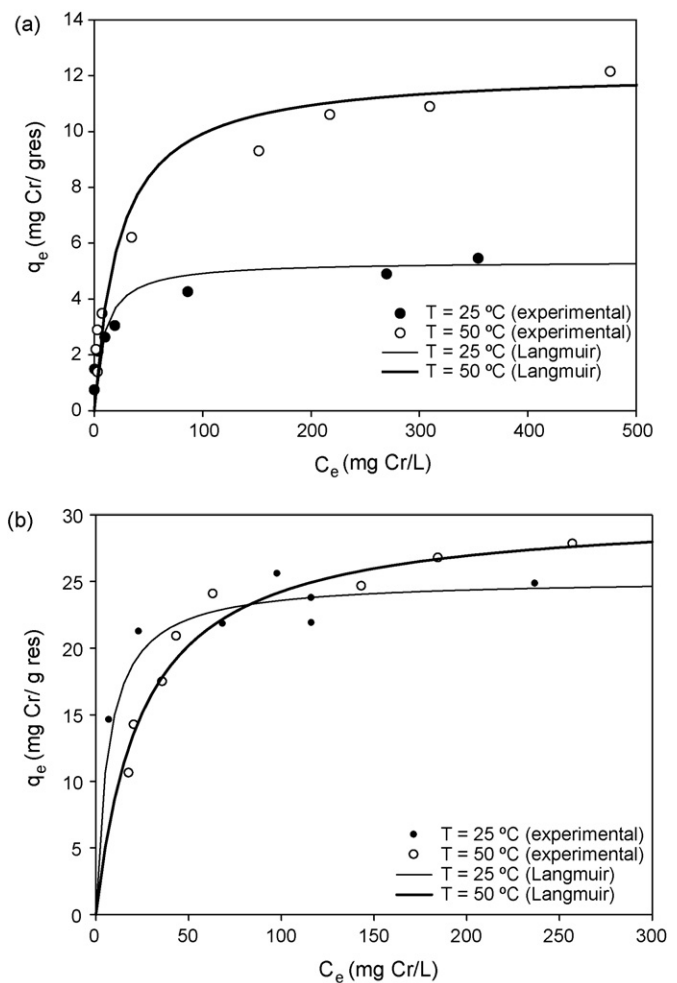


Fig. 2. Adsorption equilibrium isotherms Cr-Diaion CR11 at two different temperatures: (a) resin in the H⁺ form; (b) resin in the Na⁺ form.

Table 3
Sorption isotherm parameters for Diaion CR 11 resin

Ionic form	Parameters			
	q_{\max} (mg/g _{wet resin})	K_L (l/mg)	K_{L0} (l/mg)	ΔH (kJ/mol)
H ⁺	5.02 at 25 °C	0.130 at 25 °C	1.12×10^{-6}	–28.9
	11.5 at 50 °C	0.053 at 50 °C		
Na ⁺	24.7 at 25 °C	0.207 at 25 °C	1.03×10^{-10}	–53.1
	30.6 at 50 °C	0.039 at 50 °C		

Table 4
Differences between the initial and final pH for Diaion CR11 experiments

Ionic form	Temperature (°C)	ΔpH^a			
		$C_i = 100$ mg/l	$C_i = 400$ mg/l	$C_i = 600$ mg/l	$C_i = 800$ mg/l
H ⁺	25	–1.044	–0.969	–0.897	–0.841
	50	–1.017	–1.142	–1.094	–1.097
Na ⁺	25	5.649	1.714	1.434	1.019
	50	6.579	1.141	0.749	0.292

^a $\Delta\text{pH} = (\text{pH})_{\text{final}} - (\text{pH})_{\text{initial}}$.

between the metal and the functional groups of the resin changes with the temperature.

The Langmuir model, previously indicated in Eq. (1), in which the temperature effect follows the Arrhenius law, $K_L = K_{L0} \exp(-\Delta H/RT)$, fits well the experimental data. The parameter values estimated are shown in Table 3. The negative values of ΔH (heat adsorption) indicate the exothermic nature of the process.

We have already referred that the change of the ionic form from H⁺ to Na⁺ increases the amount of adsorbed chromium per unit of mass of resin. This effect can be verified by the ΔpH values listed in Table 4. In fact, when the resin is in the hydrogen form the pH decreases during the experience, while with the resin in the sodium form the pH increases. It is worth mention that at low pH, an excess of hydrogen ions can compete for the active sites, resulting in a lower percentage of Cr uptake. On the other hand, when the resin is converted to the Na⁺ form higher values of pH are measured in the solution and this may be a disadvantage in the presence of other metals, such the copper, which may precipitate as hydroxides.

3.3.2. Amberlite IRC86

The equilibrium experiments using Amberlite IRC86 in the Na⁺ form were performed at 25 °C. Two different effluents were tested: a synthetic chromium solution and an industrial effluent referred as sample S1, being the results given in Fig. 3.

From Fig. 3(a) it can be concluded that this resin has high adsorption capacity for chromium than the Diaion CR11 (Fig. 2(b)), and taking into account the shape of the isotherm the adsorption equilibrium can be considered almost irreversible. The Langmuir isotherm fits well the experimental data, and the parameters for this case are: $q_{\max} = 31.7$ mg/g_{res} and $K_L = 1.91 \times 10^{-1}$ l/mg. In Fig. 3(b) it can be seen that in the case of the industrial effluent the isotherm is unfavourable and

the uptake of chromium was greatly reduced due to the interference of other species in solution. This suggests that the effluent should be previously treated in order to reduce the concentration of metals such as sodium and calcium.

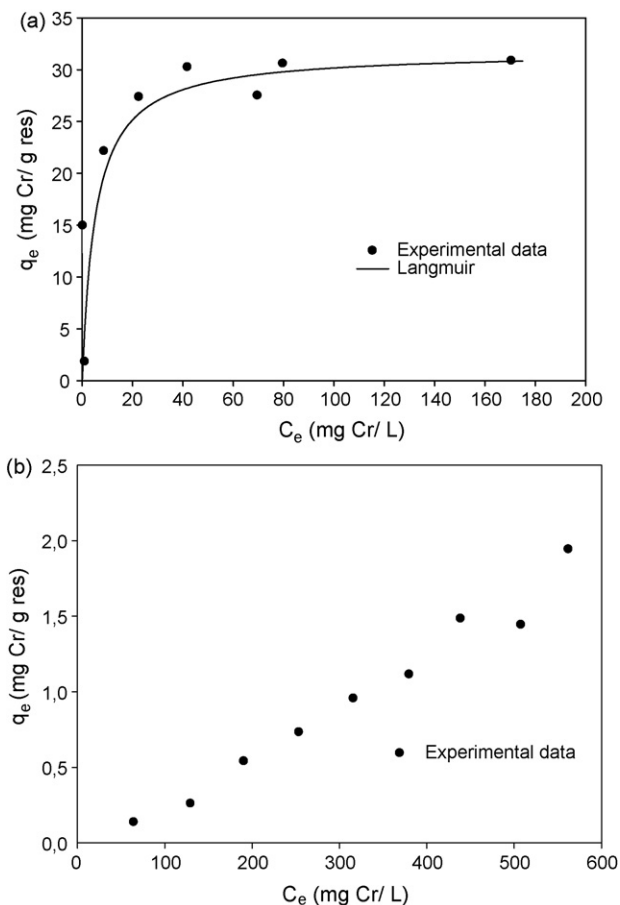


Fig. 3. Adsorption equilibrium isotherms Cr-Amberlite IRC86: (a) synthetic effluent; (b) industrial effluent.

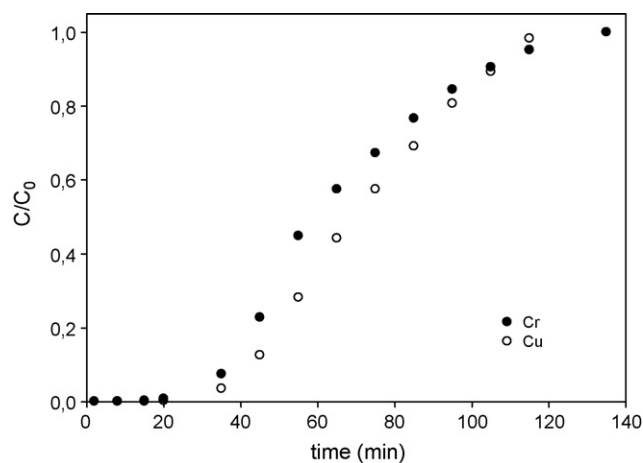


Fig. 4. Normalized concentration of chromium and copper at the column outlet as function of time.

3.4. Column experiment

A preliminary experiment in column was performed by using the Amberlite IRC86 for treating a synthetic solution containing chromium and copper, and the results are shown in Fig. 4. The chromium and copper concentrations were similar to those measured in the industrial effluent, which was previously referred as sample S1. In this figure, C and C_0 represent the concentration of the metal at the column exit and the feed concentration, respectively.

The complete saturation of the resin was achieved for a time approximately of 135 min for both metals. It can be also observed that the breakthrough curve for copper emerges almost at the same time as the one for chromium, and thus the resin has low selectivity. The sigmoid shape of the curves seems to indicate that the exchange process is controlled by the diffusion into the particle of resin.

3.5. Regeneration behaviour of the resins

In applications of cycling fixed bed operations at large scale, a crucial step of the process is the regeneration. In our study, the regeneration step was made with a solution of 1 M NaOH and 0.15 M H_2O_2 , and in both cases one may conclude that it is possible to regenerate the resins. However, future experiments should be conducted in order to optimize this important phase of ion exchange processes.

4. Conclusions

The main goal of this study was the assessment of the performance of two commercial ion exchange resins, in order to recover the chromium from industrial effluents. The tested resins were the Diaion CR11 and the Amberlite IRC86, and the experimental results showed that both are effective in the removal of chromium trivalent from aqueous solutions. The chelating resin Diaion CR11 in the Na^+ form at 50 °C exhibited higher sorption capacity, and the experimental data were well fitted by the Langmuir model. In the experiments performed with the synthetic

and the industrial effluent using the Amberlite IRC86 resin, the interference of other ions was well noted. Therefore, aiming the recovery of chromium from industrial effluents a pre-treatment should be made.

Regarding the resins regeneration, it can be concluded that both can be regenerated with a solution of 1 M NaOH and 0.15 M H_2O_2 but this is a subject to be approached in further studies.

Taking into account the overall results, one may state that the chelating resin (Diaion CR11) seems to be promising in the treatment of wastewater from electroplating industry.

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