Selective separation of Cr(III) and Fe(III) from liquid effluents using a chelating resin

Sandra Fernandes, Inês S. Romão, Carlos M. R. Abreu, Margarida J. Quina and Licínio M. Gando-Ferreira

ABSTRACT

This study aimed to assess the selective separation of Cr(III) from Fe(III) from liquid solutions by using a chelating ion exchange resin, Diaion CR 11, from Mitsubishi Chemical Corporation, in the H⁺ form. Equilibrium experiments with synthetic solutions of iron and chromium were carried out in batch mode. For both metals favorable adsorption isotherms were obtained, and the experimental data were well described by the Langmuir model. However, the resin exhibited higher affinity for iron than for chromium. The regeneration experiments revealed that, for both metals, HCl provided higher removal efficiencies than H₂SO₄ and HNO₃. Moreover, precipitation with NaOH allows selectively separate chromium and iron to be stripped from the resin. Experiments in fixed bed operation were carried out to assess the dynamic behavior of the sorption of Cr(III) and Fe(III) into the tested resin by using synthetic and industrial solutions. The experiments with industrial effluent showed that the resin can remove low levels of contaminant transition metal ions, and thus the effluent can be purified for reuse of chromium during periods of 20–25 min. The resin regeneration was achieved with a sequential treatment with HCl and NaOH/H₂O₂. High efficiencies were observed for both monocomponent and multicomponent systems. A global strategy for separating and recovering Cr(III) from an effluent that also contains Fe(III) is presented, involving the integration of ion exchange (saturation and regeneration phases) and precipitation processes. In conclusion, our approach demonstrates that efficient separation of chromium and iron is possible if ion exchange operation in a fixed bed configuration is optimized and combined with conventional processes such as precipitation.

Key words | chemical precipitation, chromium, fixed bed operation, ion-exchange, regeneration

INTRODUCTION

Many industries that use metal surface treatments in their manufacturing processes generate effluents rich in chromium and other heavy metals. Chromium is a metal widely used in the electroplating industry for both functional and decorative purposes. During the electrodeposition process, undesirable contaminants such as iron, aluminium, copper, zinc and nickel could accumulate in the plating bath. Above certain concentrations, these contaminants may cause unacceptable layer quality and reduce the bath conductivity and the cathode current efficiency as well (Darnall et al. 1993; Bayati et al. 2005).

Industrial effluents contaminated with toxic metal ions remain an important environmental issue and several methods have been used for removing them. These include chemical precipitation, ion-exchange/adsorption, membrane separation, solvent extraction and cementation (Shaalan et al. 2001; Dabrowski et al. 2004; Mohan & Pittman 2006; Mellah & Benachour 2006; Malaviya & Singh 2011). Chemical precipitation has traditionally been the most used method. This method is chemically intensive and produces considerable amounts of toxic solid residues (sludges) whose final disposal poses a challenge from the environmental standpoint. Landfills are often used for the disposal of the sludge, but the involved costs are high. Ion exchange with chelating resins is considered a better and promising alternative (Gode & Pehlivan 2003; Janin et al. 2009). Recent studies have demonstrated that these resins can be used for selective removal of chromium from

The present work aims to study the separation of Cr(III) and Fe(III) ions from aqueous solutions using a chelating resin Diaion CR 11. The recovered chromium product is suitable for reuse. The iron ion was selected as a representative contaminant for trivalent chromium electroplating baths. Equilibrium and dynamic behavior of the sorption process in column tests, using synthetic and real effluents, were investigated. In addition, the regeneration efficiencies of pre-saturated resin employing different acids and removal of Fe(III) were also assessed through precipitation tests.

MATERIALS AND METHODS

Resin and chemicals

The chelating resin Diaion CR 11 from Mitsubishi Chemical Corporation was used in this study. Resin characteristics are shown in Table 1. First, it was necessary to pre-treat the resin with repeated washings using 2 M HCl and 2 M NaOH solutions in order to remove solvents and other preparation chemicals (Manual from Mitsubishi 1995). The last step of this conditioning phase consisted of pumping a solution of HCl through the column so that the resin is converted to the H⁺ form. The excess Cl⁻ ions were removed by rinsing the resin with distilled water.

Synthetic effluent samples were prepared by dissolving an appropriate amount of chromium salt (Cr(NO₃)₃.9H₂O) and iron salt (Fe(NO₃)₃.9H₂O) in distilled water. All the chemicals used were of analytical grade and purchased from Ridel-de-Haën and Pronalab.

Batch experiments

The equilibrium isotherms were determined in batch mode. 40 mL of the synthetic solution, at different initial concentrations, were added into a flask containing 1 g of pre-conditioned resin. For Cr(III), the initial pH of these experiments was not controlled and varied from nearly 3.2 to 3.8. In the case of Fe(III), two different sets were performed: (i) uncontrolled initial pH, which varied from nearly 2.4 to 3.3; (ii) experiments with initial pH adjusted to 2 with HNO₃. Concerning the regeneration experiments, 0.25 g of pre-saturated resin samples were poured into flasks in contact with 80 mL of different acid solutions (HCl, H₂SO₄ and HNO₃) at three concentration levels (2, 1 and 0.5 M). The flasks were sealed and kept at constant temperature (25°C) in a shaker for 24 h. After equilibrium, the resin was separated by vacuum filtration and the concentrations of chromium and iron in solution were analyzed in triplicate by flame atomic absorption spectrophotometry, Perkin Elmer 3300. For quality control purposes, in the ten samples analyzed, a standard solution was introduced in order to guarantee that the calibration remained valid.

Precipitation tests were conducted in order to selectively separate metals under analysis, by adding 70 mL of 2 M NaOH into flasks containing 30 mL of supernatant solution with metal ions stripped from the resin, under continuous shaking, during 24 h. At the end of this period, that precipitated was removed by filtration and aliquots of liquid were analyzed as described above.

Column fixed bed experiments

The column tests were performed in a glass tube of 1.6 cm internal diameter and 20 cm height packed with 7–8 g of conditioned resin. Both the synthetic and industrial effluent were percolated through the column by using a peristaltic pump.
pump at a constant flow rate of 10 mL min\(^{-1}\). Table 2 summarizes the experimental conditions used in the bed saturation step. The regeneration experiments were also performed by using constant flow rate (Q) of 10 mL min\(^{-1}\) with 1 M HCl and 2 M NaOH/0.33 M H\(_2\)O\(_2\) solutions. Several samples were collected over time at the column outlet and the concentrations of chromium and iron similarly analyzed as above.

### RESULTS AND DISCUSSION

#### Equilibrium studies

Experimental and predicted data concerning the sorption equilibrium of Cr(III) and Fe(III) into resin Diaion CR11 are shown in Figures 1(a) and 1(b), respectively. According to the trends of the experimental data, all curves confirm favorable adsorption isotherms for both metals, where the amount of metal ions adsorbed per unit mass of resin increases with the metal concentration in solution as expected. In fact, experimental sorption data were well described by the Langmuir equation:

\[
q_i = \frac{q_{\text{max}, i} K_L C_i}{1 + K_L C_i}
\]

where \(q_i\) corresponds to adsorbed mass of species \(i\) (mg g\(^{-1}\) wet resin), \(C_i\) is the equilibrium concentration of species \(i\) (Cr(III) or Fe(III)) in the liquid phase (mg L\(^{-1}\); \(K_L\) and \(q_{\text{max}, i}\) are the Langmuir model parameters. The fitting of experimental data through non-linear regression analysis using SigmaPlot software enabled the parameter values shown in Table 3 to be found. According to the results reported in that table, the maximum sorption capacities for iron are always higher than the ones observed for chromium, meaning that the resin exhibits lower affinity for this metal. This achievement is not in agreement with the affinity order provided by the manufacturer on its website (www.diaion.com/en/products/chelate_01.html). Moreover, the maximum sorption capacity found for chromium (0.55 meq g\(^{-1}\)) is lower than the minimum value claimed by the manufacturer (1 meq g\(^{-1}\), considering the wet density resin = 1 g cm\(^{-3}\)) while for iron the estimated capacity (1.38 meq g\(^{-1}\)) is higher than 1 meq g\(^{-1}\). Gode & Pehlivan (2003) reported capacity values for trivalent chromium using other chelating resins based on iminodiacetate groups as follows: 1.023 meq g\(^{-1}\) for Lewatit TP 207 and 0.86 meq g\(^{-1}\) for Chelex 100.

Figure 1(b) shows that the initial solution pH has a significant effect on the Fe(III) sorption when the initial pH is adjusted to 2; the sorption capacity is lower (\(q_{\text{max}} = \)).
16.7 mg g⁻¹) than the one found (qmax = 25.7 mg g⁻¹) in the set of experiments with uncontrolled pH. Thus, the adsorption is not favoured at low pH values which may be explained by a probable competition between H⁺ and metal ions for active sites of the resin. Indeed, at high H⁺ concentrations the iminodiacetic groups of the resin matrix can react to form protonated groups which induce an electrostatic repulsion of metal ions. It is important to note that, for all experiments, the exchange between metal ions in solution and H⁺ ions bounded to the resin leads to a decrease of the pH solution. A pH variation (ΔpH = pH_initial − pH_final) from 0.7 to 1.1 was observed when the equilibrium concentration of Cr(III) was in the range of 17 to 669 mg L⁻¹. The experiments with uncontrolled initial pH for the sorption of Fe(III), showed a variation of 1.2 to 1.3 in the solution’s pH, within the range 0.4–230 mg L⁻¹, therefore confirming that the resin has major preference for ion Fe(III).

**Acid selection for resin regeneration and precipitation tests**

The regeneration step plays a crucial role in the global performance of cyclic fixed bed ion-exchange operations. Therefore, for selecting the best acid for the regeneration phase, some samples of pre-saturated resin were tested in batch mode, using solutions of HCl, H2SO4 and HNO3 at different concentrations. The obtained results are shown in Figures 2(a) and 2(b) for Cr(III) and Fe(III), respectively, where it is clearly observed that the highest removal efficiencies for both metals are achieved with HCl. The best performance of this acid in the regeneration process may be due to interactions between protonated sites of the resin and the anion associated with the acid, which leads to the formation of a complex electrical double layer close to pore surfaces (Bhandari et al. 2000). Moreover, the efficiency is affected by increasing the regenerant concentration from 0.5 to 2 M. The percentage of chromium desorbed with HCl varied from 66.52 to 79.65%, while the iron was stripped from the resin with efficiencies between 42.1 and 60.3%. The regeneration effect of H2SO4 and HNO3 solutions is much lower in the case of chromium, the efficiency values being less than 10%. On the contrary, the desorption efficiency of Fe(III) with H2SO4, for instance, varied from 30.5 to 35.7% when the acid concentration was increased from 0.5 to 2 M.

After the regeneration experiments, the supernatant solutions whose initial concentrations of metal ions are indicated in Table 4, were put in contact with 2 M NaOH in order to selectively separate chromium and iron stripped from the resin by precipitation. The results

<table>
<thead>
<tr>
<th>Regenerant Acid</th>
<th>Initial Cr conc. (mg L⁻¹)</th>
<th>Initial Fe conc. (mg L⁻¹)</th>
<th>Removal efficiency for Cr (%)</th>
<th>Removal efficiency for Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>2.0 M 47.7 3.91 0.67 90.0</td>
<td>1.0 M 47.0 3.80 0.91 90.1</td>
<td>0.5 M 31.9 2.57 0.92 90.1</td>
<td></td>
</tr>
<tr>
<td>H2SO4</td>
<td>2.0 M 4.39 2.31 2.24 85.4</td>
<td>1.0 M 3.99 2.25 2.80 85.9</td>
<td>0.5 M 3.23 2.08 3.02 86.0</td>
<td></td>
</tr>
<tr>
<td>HNO3</td>
<td>2.0 M 4.00 2.47 2.82 84.2</td>
<td>1.0 M 3.82 2.33 3.50 84.3</td>
<td>0.5 M 2.50 2.10 3.73 84.8</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2** | Regeneration of Diaion CR11 resin pre-saturated with (a) Cr(III) or (b) Fe(III) using different acid solutions.
obtained revealed high removal efficiencies for iron (85 to 90%) that precipitates as Fe(OH)₃. The low efficiencies (0.7–3.7%) achieved with the precipitation of chromium hydroxide make this a promising strategy to promote the recovery of an enriched solution of Cr(III) and its further reuse. It is worth mentioning that the optimum pH for precipitation of the trivalent chromium salt with NaOH is 8.5–9.5 (Abass et al. 2005). However, the precipitate is re-dissolved in solutions with excess of hydroxide sodium as those tested in the precipitation tests. This study enables the conclusion that higher initial ratios of Cr:Fe lead to more effective separations of the metals under analysis.

Dynamic behavior of sorption process in fixed bed operation

Experiments in a fixed bed column were performed in order to study the dynamic behavior of the sorption process of Cr(III) and Fe(III) into Diaion resin by using synthetic and industrial solutions. Monocomponent (Diaion/Cr) and multicomponent (Diaion/Cr/Fe) experimental breakthrough curves plotted as metal concentration at column outlet against time are depicted in Figures 3 and 4. From these figures, it can be observed that the saturation curves of iron emerge later than chromium as the resin has a major preference for binding Fe(III) ions, thus reinforcing the results obtained in the batch equilibrium studies. It should also be noted that when both ion metals are fed to column, multicomponent case, the stoichiometric time in the breakthrough curve of Fe(III) is more affected than in the curve of Cr(III). In addition, the kinetic behavior of the sorption of iron is also changed in the presence of chromium and less time is required for achieving saturation conditions. The ion-exchange capacities determined from saturation curves were 10.2 and 8.8 mg g⁻¹ for Diaion/Cr and Diaion/Cr/Fe systems, respectively. Thus for chromium ion, there was only a 14% decrease in the bed capacity during the multicomponent saturation compared with the monocomponent experiment.

The breakthrough curves for chromium, iron and copper concerning the treatment of an industrial effluent, generated by a hard chromium electroplating industry, are shown in Figure 4. In addition to Cr and Fe ions,
this effluent also contained Cu, Ni, Pb, Na, K, Ca and Mg whose concentrations were 2.4, 0.4, 4.2, 53.9, 3.3, 115.0 and 15.2 mg/L, respectively. By analyzing the results presented in Figure 4, it can be concluded that the resin selectively removes low levels of contaminant transition metal ions (Fe and Cu) from solutions with high concentrations of the desired trivalent chromium even in the presence of moderate concentrations of alkaline and earth alkaline metals. It should be noted that the performance of chelating resins, such as Diaion CR11, are not affected by the presence of alkaline and earth alkaline metals. So, the industrial effluent can be purified for reuse in a chromium electroplating bath during an operation period of 30 min corresponding to the breakpoint time (t_{BP}) for the saturation curve where the iron concentration is equal to 5% of its feed concentration. In addition, the recovery rate \( \left( \frac{Q_{Cr}^{feed}C_{Cr}}{Q_{Cr}C_{Cr_{BP}}} \times 100 \right) \) of chromium until t_{BP} was 53.5%.

Experimental elution curves for chromium and iron as a function of time are depicted in Figures 5(a) and 6(a). These regeneration processes were performed in a sequential way using 1 M HCl followed by 2 M NaOH/0.33 M H2O2 solution. In fact, it is well known that the regeneration of cationic resins loaded with trivalent chromium using HCl and NaOH/H2O2 for Cr(III) and Fe(III) is depicted in Figure 5. Figure 6 illustrates a global strategy for recovery of Cr(III) from effluents with Cr(III)/Fe(III).
conventional chemicals (e.g. mineral acids or saline solutions) is very difficult. A prolonged period of contact between the resin and an acid promotes the formation of hydrolyzed and surface-precipitated hydroxi-Cr(III) species that are irreversibly adsorbed (Yalçin et al. 2001). The use of a mixture of NaOH/H2O2 as a regenerant seems to be a promising alternative to strip Cr(III) from the resin (Petruzelli et al. 1995). In alkaline conditions, the oxidation of Cr(III) to Cr(VI) into its anionic form CrO4^2−, that is rejected by the cationic resin due to the Donnan effect, may be obtained according to the following reaction:

\[
2(RCOO)\text{Cr} + 3\text{H}_2\text{O}_2 + 10\text{NaOH} \\
\rightarrow 2\text{Na}_2\text{CrO}_4 + 8\text{H}_2\text{O} + 6(RCOONa)
\]  

Equation (2)

For the system Diaion/Cr, Figure 5(a) shows that, during the resin regeneration with HCl, the elution curve reached a concentration peak of 1,160 mg L^−1 (2.4 times higher than initial concentration) applying 5.4 BV (18 ± 12 cm³) of regenerant solution, which corresponds to 6–7 min of regeneration time. After this period of time, the concentration decreases sharply to 5 mg L^−1 at 18 min, and then a very small change in concentration occurs being its final value of 4 mg L^−1 at 58 min (≈52 BV). The elution with NaOH/H2O2 resulted in a concentration peak of 528 mg L^−1 at 7.1 BV. Hence, regeneration efficiencies of 54 and 19% were observed for Cr during the first and second elution steps, Figure 5(c), giving an overall efficiency of 73%. In the case of Diaion/Fe system, the iron ion was stripped from resin with high efficiency (around 91%) using only one step with HCl as shown in Figure 5(d). In Figure 5(b) it can be noticed that a concentration peak of 343 mg L^−1 (20.4 times higher than initial concentration) is reached with 11.6 BV (at nearly 15 min) of used acid. By comparing the elution curves of both metals, it can be concluded that the maximum concentration occurred later in the case of iron because the resin has higher affinity for this species.

The regeneration behavior of the resin was changed when the bed resin was pre-saturated with the binary mixture Cr(III)/Fe(III). The concentration factors in the peaks of the respective elution curves were 1.9 and 8.1 for chromium and iron, during the regeneration step with HCl. The overall efficiency of removal for chromium was 97% (52 and 45% for the first and second regeneration steps). This value is 1.3 times higher than the efficiency calculated for the system Diaion/Cr probably due to the catalytic effect of iron on the oxidation reaction of the trivalent chromium species, Equation (2). In the case of iron, the global efficiency of removal was 99% (55 and 44% for the first and second regeneration steps).

**Strategy for the selective separation of Cr(III) and Fe(III)**

As mentioned previously the main objective of this study was to assess the possibility of selectively separating Cr(III) and Fe(III) by using a chelating ion exchange resin, in order to recover Cr(III) for further reuse. According to the data discussed in the previous sections, Figure 6 summarizes a possible strategy to accomplish this objective.

The approach proposed here consists of treating the stream A (industrial effluent) containing 470 mg/L of Cr and 17 mg/L of Fe, in a fixed bed column packed with Diaion CR 11 resin. Based on the results shown in Figure 4(a) and (b), it is possible to collect a B’ stream enriched in chromium (340 mg/L of Cr and 0.4 mg/L of Fe) during a period between 10 and 30 min of the resin saturation, which can be further recovered. The saturation phase is stopped when the breakpoint time for iron is reached, its concentration at that instant being equal to 5% of the feed concentration. Then, the regeneration of the bed begins and a stream C’ can be recovered with very high concentration of Cr(III) (580 mg/L of Cr and 3 mg/L of Fe) in the first 8 min of operation using HCl as regenerant, because the elution of chromium occurs before iron as observed in Figures 5(a) and (b). The stream C should be treated by chemical precipitation with excess NaOH and its average composition (130 mg/L of Cr and 30 mg/L of Fe) was estimated through mass balances considering the two regeneration steps. It was assumed that the second regeneration with NaOH/H2O2 starts after 20 min has elapsed from the first regeneration step. Therefore, the stream C is composed by solution coming from this step between 8 and 20 min, as well as solution collected during 20 min of operation of the resin regeneration with NaOH/H2O2. Finally, considering a removal efficiency of 90% for iron in the treatment of C, Fe(OH)₃ precipitate may be obtained in D by filtration, and a chromium solution with high purity (≈130 mg/L) in stream D’. In short, it is possible to conclude that the approach schematized in Figure 6 promotes an overall recovery rate close to 100% for chromium salt that can be reused in the electroplating process.

The economic evaluation of the global treatment for recovery of chromium depends on facilities (equipment), operating costs and savings. The operating costs are mainly related to chemicals for regeneration and
precipitation, labor and maintenance, resin replacement, energy and utilities. Thus the benefits of the strategy indicated in Figure 6 enable savings of raw materials (chromium salts), water and wastewater treatment. Moreover, this strategy significantly lowers the environmental impact when compared with the conventional treatment, as the recovery of Cr(III) is promoted instead of formation of sludge that requires disposal in a landfill site.

CONCLUSIONS

This study aimed for the selective separation of Cr(III) from Fe(III) by using a chelating ion exchange resin (Diaion CR 11) in the $\text{H}^+$ form. The liquid effluent tested involved higher concentration of Cr(III) than Fe(III), in order to simulate a real effluent from an electroplating industry. The investigation involved experimental equilibrium studies and dynamic behavior analysis of ion exchange process in a fixed bed operation.

The sorption equilibrium of Cr(III) and Fe(III) into the resin revealed favorable adsorption isotherms for both metals, that were well described by Langmuir model. The resin revealed favorable adsorption isotherms for both metals and the maximum sorption capacity for iron is higher (25.6 mg g$^{-1}$) than the one observed for chromium (10.0 mg g$^{-1}$). The resin regeneration was tested with HCl, H$_2$SO$_4$ and HNO$_3$ at different concentrations and the results revealed that the highest removal efficiency for both metals is achieved with HCl.

Monocomponent and multicomponent fixed bed experiments disclosed that the saturation curves of iron emerge later than chromium as the resin has a greater preference for binding the former ions.

The regeneration phase was carried out in a sequential way using 1 M HCl followed by 2 M NaOH/0.33 M H$_2$O$_2$ solution. The elution curves indicated that high efficiencies of regeneration can be reached for both metals, and the maximum concentration occurred later in the case of iron because the resin has higher affinity for this species.

Based on the experimental data of this study, a possible strategy to accomplish the recovery of chromium was proposed which involves the integration of both fixed bed ion exchange and precipitation processes. In fact, a stream with high content of Cr(III) and almost free of Fe(III) may be collected during the saturation and regeneration phases as well as by selective precipitation with NaOH.

In conclusion, the approach proposed in this study allows the efficient separation and recovery of chromium from liquid effluents contaminated with iron simultaneously solving two of the main problems related to the electroplating industry: the loss of valuable raw materials and the treatment of hazardous effluents for the environment.

ACKNOWLEDGEMENTS

We would like to thank FCT (Foundation for Technology and Science) for its financial support for this work (Project: POCTI/EQU/58149/2004).

REFERENCES


Mellah, A. & Benachour, D. 2006 Solvent extraction of heavy metals contained in phosphoric acid solutions by 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline in kerosene diluent. Hydrometallurgy 81 (2), 100–103.


First received 1 March 2012; accepted in revised form 28 May 2012