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Selective separation of chromium (III) from electroplating effluents by ion-exchange processes

S. Fernandes, S. A. Cavaco, M. J. Quina and L. M. Gando-Ferreira

GERSE - Group on Environment, Reaction and Separation Engineering, Department of Chemical Engineering, University of Coimbra, Pólo II, Rua Sílvio Lima, 3030–790 Coimbra, Portugal.

Abstract

This work reviews the application of the ion-exchange technology to treat industrial effluents containing heavy metals and presents results on the uptake of Cr (III) from aqueous solutions using the polyfunctional chelating exchange resin Diphonix. Some industrial samples of effluent collected in an electroplating industry were characterized in what respects metals, total suspended and dissolved solids (TSS, TDS), chemical oxygen demand (COD) and pH. In order to evaluate the sorption capacity of the resin, some batch equilibrium experiments were carried out. The effects of temperature and the presence of acid nitric in solution on the ion-exchange equilibrium were studied, and it was observed that the sorption capacity of the resin is affected by both variables. Moreover, saturation experiments in column were also performed in order to determine the dynamic behaviour of the process. The results suggest that the resin tested offers a good performance towards the Cr(III) removal and can be easily regenerated with a mixture of NaOH and H_2O_2.

Keywords: Chromium; Ion-exchange; electroplating effluent; Diphonix

1. Introduction

Chromium is a common pollutant found in a variety of industrial effluents mainly as Cr(III) or Cr(VI), including those from metal working industries such as the electroplating, as well as tanning of leather and pigments manufacturing. The separation and recovery of the chromium from these effluents should be assured for environmental protection and economic reasons. Indeed, from the environmental viewpoint, this metal is usually considered very toxic for humans, animals and even plants, being the hexavalent form potentially carcinogenic when inhaled. Indeed, chromium has been found to cause adverse effects for offspring when given to pregnant animals, having a significant teratogenic potential. As regards the economic issue, the chromium may be recovered from the treatment of electroplating rinses and

wastewater of high concentration in order to be reused in the plating process, being thus possible to improve the global process economy.

The conventional techniques in use for metal control are based on chemical precipitation coupled to pre- or post-oxidation/reduction and followed by filtration. The main disadvantage of these techniques is the production of large volumes of hazardous residues (sludges), which are difficult to handle. In fact, these sludges may be unstable and costly to dispose of as it. Ion-exchange processes have been frequently used as an effective alternative technique for the treatment of industrial effluents containing heavy metals and for the recovery of the valuable components. Some studies have been published reporting heavy metals removal using ion-exchange resins [1-19]. In fact, the selective removal by ion-exchange of Pb(II), Hg(II), Cd(II), Ni(II), V(IV,V), Cr(III,VI), Cu(II) and Zn(II) from waters and wastewaters was recently reviewed [19].

Park and collaborators studied the adsorption behaviour of several ions in the Amberlite IRC 748 (formerly IRC 718), a chelating resin, and evaluated the separation and preconcentration of Au(III) as their chloro complexes from acidic solutions in a column [9]. They concluded that this resin has good potential for the enrichment of platinum group elements (Au(III) Pt(IV) and Pd(II)) and their separation from other metal ions. Amberlite IRC 748 was also used in other studies, such as for the removal of Cu(II) and Zn(II) [10]. In this study, the performance of Amberlite IRC 748 is compared with Chelex 100 (also a chelating resin), and the main conclusion was that the amount of metals exchanged using IRC 748 was greater than Chelex 100 (comparable conditions).

Pramanik et al. synthesized a chelating resin containing azophenolcarboxylate functionality, and evaluated the selectivity of the resin for Cr(III) and Cr(VI) [11]. Their results showed that Cr(III) is selectively retained at ca. pH 5.0 and Cr(VI) at ca. pH 2.0 which indicates that, in column, the new material is able to separate Cr(III) from Cr(VI). For removal and recovery of Cr(VI) from polluted ground waters Galán and co-workers studied three alternatives, which comprehended anion-exchange resins, liquid-liquid extraction assisted by hollow fiber membranes and emulsion pertraction [12]. From their study they concluded that the anion-exchange resins and the emulsion pertraction lead to higher velocities of chromium removal.

Cationic exchange resins have been widely used aiming the removal and recovery of several metals, and good performances have been achieved [13-16]. One of the major problems of ion-exchange processes is related with the regeneration of the resin. A new regeneration method based on the principle of electrodialysis was proposed, and the capacity of an anion exchange resin was restored in 93% [17]. During the ion-exchange process, the resin matrix may be changed, and some studies indicate the chemical degradation over 25 repeated cycles [18].

In the present study was tested a polyfunctional chelating ion exchanger containing both sulfonic and phosphonic acid groups, Diphonix resin (Eichrom Europe), which has strong affinity for Cr(III), Fe(III) and Ni(III) in acidic solutions as reported elsewhere [20, 21]. Batch equilibrium experiments and tests in column were carried out to evaluate the sorption performance of the resin. The chromium solutions employed in these experiments were industrial effluent samples and synthetic solutions.

2. Experimental Procedures

For evaluating the selective separation of chromium from electroplating effluents by ion-exchange process, several experiments were performed, which included industrial effluents characterization, resin characterization, as well as equilibrium, saturation and regeneration tests.

2.1 Characterisation of industrial effluents

Six samples of an industrial effluent were collected from a chromium electroplating industry, which performs electroplating in plastic pieces mainly for bathroom use. The samples were collected from batch plating baths.

The elemental content of Cr, Cu, Ni, Na, Ca and Fe in these samples were quantified by Flame Atomic Absorption Spectrophotometry (FAAS), Perkin Elmer 3300, with a flame of air-acetylene. The Total Suspended Solids (TSS) were determined as the amount of solids that is retained by a filter with a pore size of 0.45 µm. The Total Dissolved Solids (TDS), although may be estimated from the electrical conductivity, in our study was determined by evaporating a certain volume of effluent (50 mL) at 103ºC, and re-weighting the crucible. The Chemical Oxygen Demand (COD), being a quantitative assess of the amount of oxygen required for the chemical oxidation of organic material, was measured by using kits of CSB 1500/ COD 1500 from WTW. The measurement of pH was carried out electrometrically using a pH meter, WTW pH-electrode SenTix 21.

All the reagents used in this study were of analytical grade and were obtained mainly from Riedel-de Haën.

2.2 Ion exchange resin

Diphonix resin (Eichrom Europe) which is a polystyrene/divinylbenzene matrix in spherical beads form was used in this study. This is a polyfunctional chelating ion exchanger constituted by diphosphonic and sulfonic acid groups bonded to the polymer matrix. The moisture content of the resin was measured as the difference of weight between a certain amount of resin before and after being dried at 103 ºC.

In what concerns the apparent density, ρ_{ap}, it was obtained from the real density of the wet resin sample (evaluated by the displacement of *n*-heptane in a picnometer) and the moisture content. The wet particle porosity, ε, was evaluated considering the real and apparent densities.

2.3 Equilibrium isotherms and regeneration

The ion-exchange isotherms for Cr(III) were achieved in batch mode at 25 ºC, in which 1 g of resin was contacted with 40 mL of a solution prepared with Cr(NO$_3$)$_3$ at different initial concentrations, for 24 h. At the end, the concentration of chromium in the solution was measured through FAAS.

The regeneration of the column saturated resin was also performed in batch mode at 25 ºC, but in these cases 80 mL of solution were placed in contact with 0.5 g of

resin. Aiming the resin regeneration, different acids (HCl, HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$) at 1M and 2M, and a mixture of 1M NaOH and 0.33M H$_2$O$_2$ were tested.

The equilibrium isotherms and regeneration process was studied only based on synthetic solutions.

2.4 Column experiments

To study the saturation process, some column experiments were fulfilled using synthetic and industrial effluent. In these experiments, a flowrate of 10 mL/min was passed through a column with an internal diameter of 1.6 cm by using a peristaltic pump. The mass of resin used was approximately 8 g. The breakthrough curves were obtained by analysing the metal concentrations in the fractions of effluent collected along the time.

3. Results and Discussion

This study was focused on the evaluation of the selective separation of chromium (III) from electroplating effluents. Therefore, some experiments concerning equilibrium, saturation and regeneration were performed. In addition, some industrial effluent samples were characterized, in order to determine the most important parameter as well as their variability, which may determine the performance of ion-exchange process. Also some characteristics of the resin used in the study were determined.

3.1- Characterization of industrial samples

Six samples (S1 to S6) of industrial effluent generated from an electroplating plant were characterized during 6 months, in terms of the most significant metal content, TSS, TDS, pH and CQO. The metals analysed included Cr, Cu, Ni, Fe, Na and Ca, and the concentrations measured are indicated in Figure 1(a)-(b). The chromium concentration in these samples ranged from 50 (in S2) to 2300 mg/L (in S1), and since FAAS was used these values are referred to total concentrations. This broad range of concentrations may create difficulties for ion-exchange processes, and in some cases previous dilution will be needed.

The concentration of Cu, Ni, Na, Ca and Fe are lower than 50 mg/L for all samples, Figure 1(b). Therefore, the main metal of concern in this type of effluent is chromium, and the ion-exchange technique may be used for recovering purposes. However, the performance of this process depends also on other parameters, such as Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD). In fact, the TSS measured for all samples of industrial effluent are in a range that do not require pre-filtration, since the determined amounts were lower than 20 mg/L. In what respects COD, and as expected, their observed values were lower than 100 mg O$_2$/L. The TDS correspond to the sum of the concentration of soluble compounds found in effluent samples, and as observed in Figure 1(c), the values are lower than 2.5 g/L (due to logistic problems, this parameter was not determined for S1). Figure 1(d) shows the pH of industrial samples, being possible to observe that the effluent has always acidic characteristics. This range for pH is adequate to the ion-exchange process.
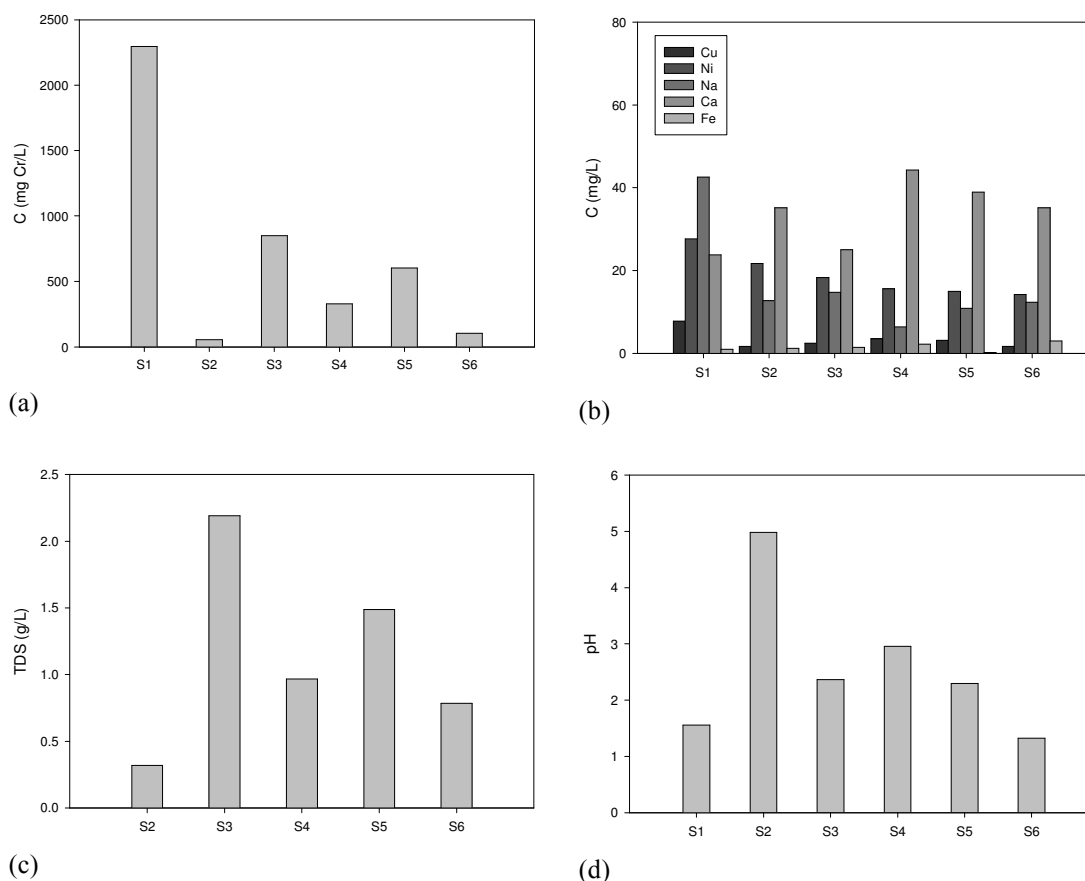
Figure 1- Characterization of six (S1 to S6) industrial effluents (a) - Cr concentration; (b) - Cu, Ni, Na, Ca and Fe concentrations; (c) - Total Dissolved Solids; (d) - pH.

3.2- Characterization of Diphonix resin

The resin used in this study is a polyfunctional chelating ion exchanger and is commercially known as Diphonix. Some samples were characterized and was determined that the resin is characterized by a moisture content of 58.3%, an apparent density, ρ_{ap}, of 0.39 g dry resin/cm^3 wet resin and a wet intraparticle porosity, ε_p, of 0.70. This particular resin doesn't present swelling when in contact with the solution in study.

3.3- Equilibrium experiments

The sorption isotherms for Cr (III) were experimentally determined at two different temperatures (25 and 50ºC). The obtained equilibrium data from batch experiments without nitric acid are shown in Figure 2(a), and the sorption data suggests a rectangular isotherm, which is typical of irreversible ion-exchange processes. This behaviour is well described by the Langmuir model:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{1}$$

where q_e is the amount of Cr adsorbed in the resin (mg/g$_{wet\ resin}$), C_e is the equilibrium concentration (mg/L), q_{max} is the maximum content of Cr that can be adsorbed on solid phase (mg/ g$_{wet\ resin}$) and K_L is the equilibrium constant (L/mg).

By fitting the model to the experimental data, it was found the isotherm parameters as being: q$_{max}$ = 19.73 mg Cr/g$_{wet\ resin}$ and K$_L$ = 0.59 L/mg Cr, at 25 ^{o}C. For the case where the temperature was kept at 50 ºC, q$_{max}$ is 27.02 mg Cr/ g$_{wet\ resin}$ and K$_L$ is 0.297 L/mg Cr. These results show that the sorption capacity of the resin Diphonix is affected by the temperature change.

The effect of initial HNO$_3$ concentration was also examined, and the equilibrium data are represented in Figure 2(b). These data show that the amount adsorbed in the resin is strongly dependent on the acid concentration. Indeed, the uptake of Cr(III) decreases as acid concentration until 3-4 M HNO$_3$, and then increases.
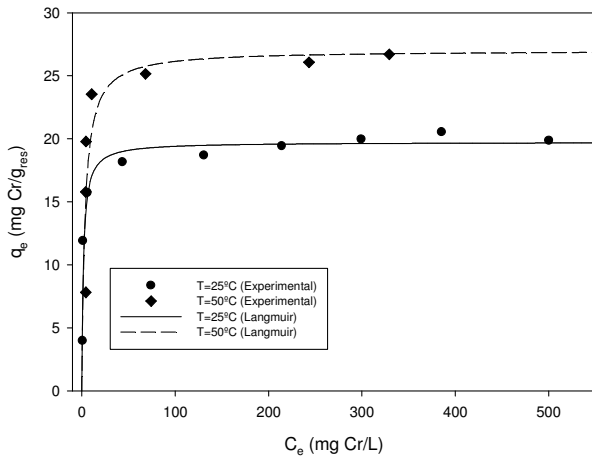
(a)

Figure 2a – Ion-exchange equilibrium isotherms at two different temperatures.
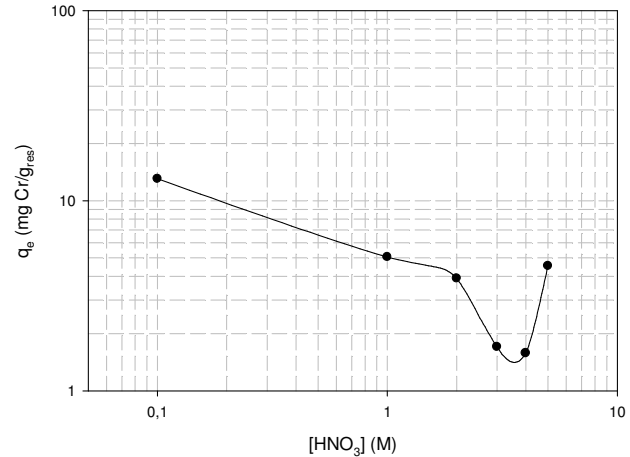
(b)

Figure 2b – Effect of acid nitric on uptake of Cr(III) by the resin Diphonix

3.4- Saturations of the resin in column

As referred above, the saturation process was studied using a column previously filled with approximately 8 g of resin. The experiments were performed using synthetic solution with an initial concentration of 530 mg Cr/L, and industrial sample (S6) with 104 mg Cr /L, 3.0 mg Fe /L and 15.0 mg Ni/L. The breakthrough curves are shown in Figures 3 and 4, respectively, indicating that the uptake of chromium by the resin decreased in the case of the industrial effluent. This behaviour results from the interference of other species in solution. However, the passage of the effluent through the resin reduces significantly the concentration of the contaminants being possible to reuse in the electroplating process the solution of chromium collected at outlet of the column during around 100 minutes.
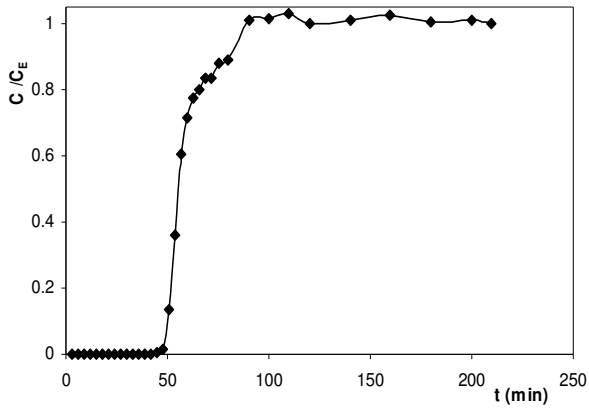
Figure 3- Experimental breakthrough curve for the system synthetic solution / Diphonix.
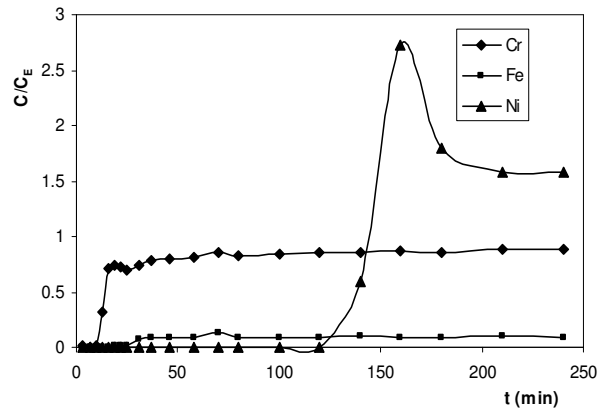

Figure 4- Experimental breakthrough curves for the system industrial effluent / Diphonix.

3.5- Regeneration experiments

The reliability of the ion exchange process strongly depends on the regeneration efficiency. In fact, if a resin is characterized by high selectivity but low regeneration capacity, the overall process is then less attractive. The process of regeneration was studied in batch experiments and different acids (HCl, HNO_3, H_2SO_4 and H_3PO_4) at 1 and 2 M of concentration, as well as a mixture of 1M NaOH and 0.33 M H_2O_2 were tested. The main results obtained concerning the percentage of the Cr released were plotted in Figure 5. In what regards the acidic solution, it was observed that a slightly high recover is observed for concentration of 2M.
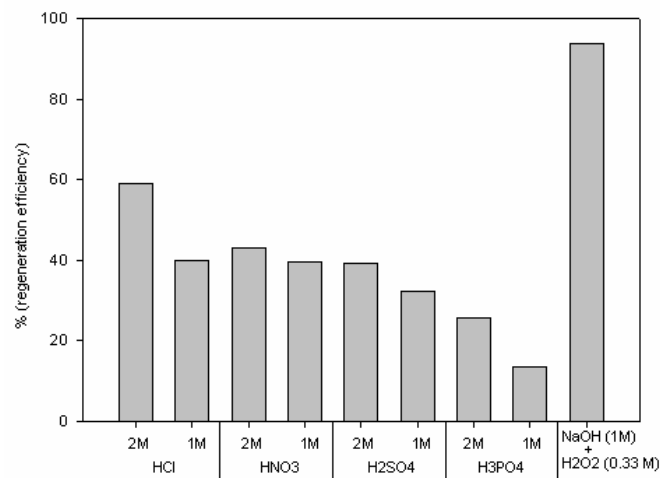

Figure 5- Regeneration of the Diphonix resin with different liquid solutions.

However, these results clearly show that using NaOH and H_2O_2 is more effective than the others to strip Cr (III) from the resin. The efficiency of this regenerant may be justified by the oxidation in alkaline medium of Cr(III) to Cr(VI) as CrO_4^{2-} which is rejected by the cationic resin.

All the results indicated in Figure 5 were obtained for 25ºC, and although not indicated on there, the mixture of NaOH and H_2O_2 was also tested for 60ºC. In this case the amount of strip Cr is slightly higher (96.3 % instead 93.7 %), but the difference do not justify to perform regeneration at higher temperature.

Conclusions

The main objective of this study was to evaluate the selective separation of Cr(III) from electroplating effluents by using a polyfunctional chelating ion exchanger resin. From the characterization of the effluent along 6 months, the main conclusions were that the main metal of concern in this effluent is Cr, which one may be present in a wide range of concentrations. In some cases, the effluent may need of a pre-dilution before be introduced in ion-exchange process. The effluent is also characterized by acidic pH, with low TSS and COD.

The equilibrium isotherm were well fitted by the Langmuir model, and the Diphonix resin reveals a sorption capacity which is affected by the temperature and strongly dependent on the acid concentration in solution.

From the saturation column experiments, it was observed that the uptake of chromium by the resin decreased in the case of the industrial effluent, being this behaviour a result from the interference of other species in solution. Nevertheless, the passage of the effluent through the resin reduces significantly the concentration of the contaminants during around 100 minutes, being then possible to reuse in the electroplating process the solution of chromium collected at outlet of the column.

High regeneration efficiencies of the Diphonix resin were obtained by using a mixture of NaOH and H_2O_2 to strip Cr (III) from the resin. In this case, little influence is observed when high temperatures were tested.

The results of this study suggest that the Diphonix resin offers a good performance towards the Cr(III) removal.

Acknowledgements

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