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Recovery of chromium(VI) from hydrochloric acid liquors using the resin Dowex 1×8

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The adsorption of chromium(VI) on the Dowex 1×8 resin has been studied. The influence of several variables such as the temperature, the hydrochloric acid and metal concentrations in the aqueous phase and the variation of the amount of resin added has been investigated. Various aqueous solutions were used for the elution of the metal. Although concentrated nitric acid elutes chromium, this can be best accomplished using hydrazine sulfate solutions which at the same time reduce the toxic Cr(VI) to the less toxic trivalent chromium state. Results obtained from batch experiments were applied to a continuous system using vertical columns. Furthermore, the methodology was transferred to an on-line flow injection system.

Keywords: chromium (VI), Dowex 1×8 resin, hydrochloric acid

Introduction

The toxicity of chromium(VI) is well known, thus its elimination from effluents is a primary target in industrialised countries, and the use of various techniques for the removal of chromium from wastewaters is described in the literature.[1]

Among the the various separation operations, the use of solvent extraction, membrane technologies and ion exchange had been described.[2-7] In many cases, the adsorption of a solute in a solid support has the claimed advantages over solvent extraction in that no mixing and settling requirements have to be fulfilled and there is no organic phase loss *i.e.* entrainment is avoided.[8,9]

On the other hand, for analytical purposes solid–ion exchange separation can be used for matrix separation, to eliminate interelement interferences, as well as a preconcentration technique to achieve better precision and lower determination limits. In previous work, the speciation of chromium in steelmaking solid wastes using Dowex 50W and Dowex 1×8 resins was accomplished.[10]

Since hexavalent chromium present in wastewaters is mainly in the form of anionic species (chromate or dichromate ions), in the present work the adsorption and elution of chromium(VI) from hydrochloric acid solutions were investigated using the anionic exchange resin Dowex 1×8. The influence of various parameters affecting the metal adsorption on the resin are studied, whereas metal elution from the loaded resin is studied using either nitric acid or reducing agents to accomplish, in this last case, both the metal elution and the reduction to a less toxic form (chromium(III)). The procedure was finally transferred to an on-line flow injection system.

Experimental

The ion exchange resin Dowex 1×8 (Fluka) was used to adsorb chromium(VI) from hydrochloric acid solutions. Dowex 1×8 is a strongly basic anion exchanger containing a trimethylammonium active group (Cl^- form). It was used for chromium adsorption without pre-treatment. The micrographs of the resin obtained by scanning electron microscopy, presented in Fig. 1, show an uniform structure. Its lack of surface porosity makes Dowex 1×8 a gel type resin and its surface area is large as the particle size is heterogeneous and relatively small (150–300 μm). Aqueous Cr(VI) stock solution was prepared from solid $K_2Cr_2O_7$ (Merck), whereas working solutions were prepared by dilution. Other chemicals used in the present investigation were of AR grade.

Batch adsorption experiments were carried out by mixing in a glass reactor weighed amounts of resin with the aqueous metal solution for the appropriate time. The remaining metal in the aqueous phase was determined by atomic absorption spectrometry and the amount of metal loaded on the resin phase was calculated by applying the mass balance.

For the study of adsorption or elution in continuous systems, two types of columns were used: a mini-glass column (internal diameter 0.8 cm), provided with porous frits, filled with 0.5 g of resin and micro-columns (made from PTFE tubing typically with an internal diameter of 0.2 cm and filled with a volume resin of 125 μl) were fed with the corresponding aqueous solutions. Samples were regularly collected and analysed.

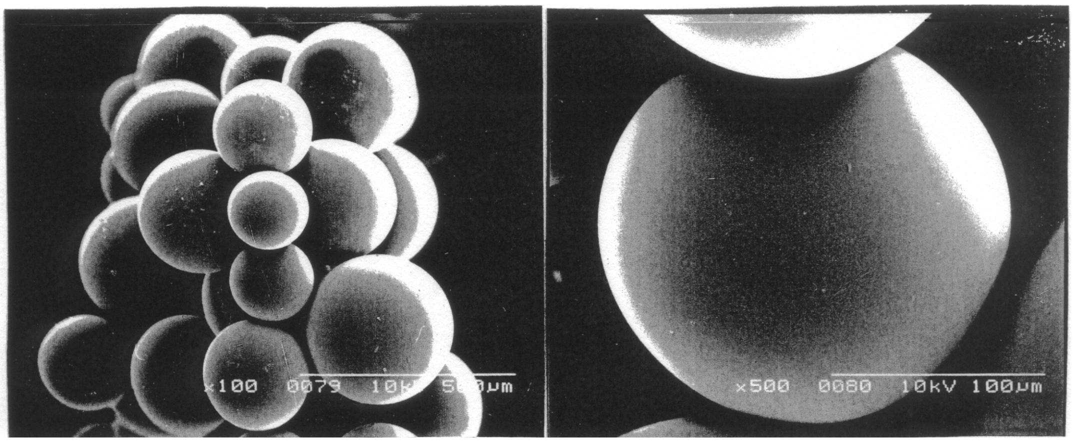

Fig.1 Scanning electron micrographs of the Dowex 1×8 resin beads.

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After operating the continuous systems by using the vertical mini-columns the procedure was transferred to an on-line flow injection system by using a micro-column integrated in a FI manifold system.

Experimental reproducibility was verified by duplication.

Results and discussion

Chromium adsorption: Batch experiments: Resin of 0.17 g/l was used to adsorb chromium(VI) from a solution of 10 mg/l Cr (300 ml) with the agitation speeds of 500, 750 and 1100 rpm. Figure 2 indicates that the chromium adsorption was significantly dependent on agitation speed with a maximum metal load at 750 rpm. This results show that at this speed an interparticle or mixed diffusion-controlled process occurred, whereas at agitation speeds of 500 and 1100 rpm the adsorption process can be attributed to an external film diffusion-controlled mechanism.[11] A speed of 750 rpm was chosen as the standard testing condition.

The adsorption isotherm of Dowex 1×8 was determined at 20°C in a 300 ml solution containing an initial concentration of 10 mg/l Cr(VI) at 0.5 M HCl for 3 hours. Concentrations of 1.3, 0.67, 0.33 and 0.17 g/l of wet resin were used. Under these conditions, increasing the volume of resin gave an increasing in chromium adsorption and a plot of log $[Cr(VI)]_{resin}$ versus log $[Cr(VI)]_{aq}$ was linear as described by the Freundlich equation,[12,13] (log $[Cr(VI]_{resin}$= log K + *n* log $[Cr(VI)]_{aq}$ with r^2= 0.995 at the present experimental conditions) and where $[Cr(VI)]_{resin}$ is resin loading, $[Cr(VI)]_{aq}$ is equilibrium concentration; n and K are constants. The experimental results of n and K values for the chromium adsorbed on Dowex 1×8 were 0.63 and 9.8 respectively. Thus, the resin loading would be 2.3 mg/g at an equilibrium concentration of 0.1 mg/l.

The influence of the initial chromium concentration on metal loading was studied by adding 0.1 g resin to a 300 ml solution containing 40, 20, 10 and 5 mg/l Cr at 20°C with an agitation speed of 750 rpm, with results showing that the adsorption rate was fast at the initial stage: more than 70% of chromium was adsorbed in 30 min with the resin loading approaching a plateau after 1 h contact with the solution. More than 90% of chromium was adsorbed by the resin within 1 h of contact for all initial chromium concentrations. The resin loading ranged from 8.7 to 47.1 mg/g depending on the initial chromium concentration.

The effect of resin concentration on metal loading was also studied. Concentrations of 0.17, 0.33, 0.67 and 1.3 g/l resin were used to contact a 300 mL solution containing 10 mg/l Cr(VI) at 20°C at an agitation speed of 750 rpm. Results obtained (Fig.3) showed that there seems to be a smooth dependence of adsorption curves upon concentration, the resin of 0.67 and 1.3 g/l adsorbed more than 90% of chromium from the solution in near 30 min with a resin loading of 12.5 and 7.1 mg Cr/g resin, respectively. On the other hand, the chromium adsorption using a concentration of 0.17 g/l resin was 70% and 84% in 15 and 30 min, respectively, with a resin loading of 21.3 and 25.5 mg/g. It seems obvious that a minimum resin concentration of 0.67 g/l is required to have a better adsorption kinetic.

The kinetics of resin loading were investigated at 20°C, 35°C and 50°C using 0.33 g/l resin in a solution of 10 mg/l Cr(VI) with 750 rpm; with the increase of solution temperature the chromium adsorption was diminished and the desorption process slowly began. Hence, the operating temperature of the resin adsorption should not be higher than 20–25°C, 20°C was used as the standard testing condition.

The influence of the presence of HCl in the aqueous solution was also studied using HCl concentrations ranging from 0.12 to 4 M. Maximum resin loading is obtained with 0.5 M HCl, decreasing the metal loading in the resin either at lower or higher acidic concentrations.

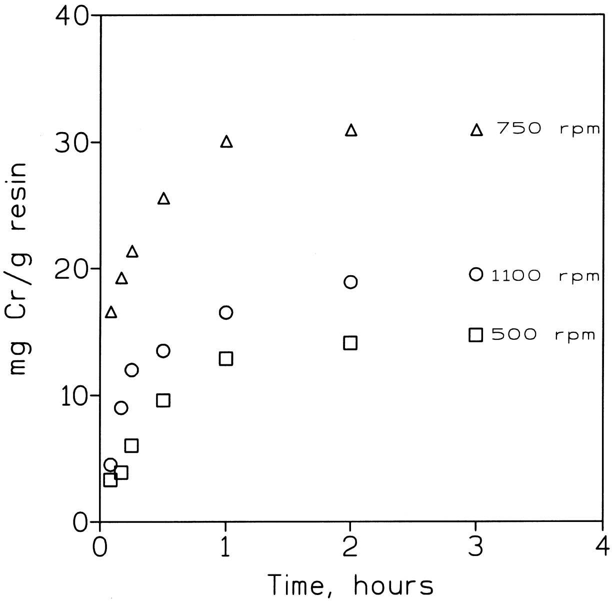

Fig.2 Effect of stirring speed on loading kinetics. Initial solution: 0.5 M HCl. Temperature: 20°C.

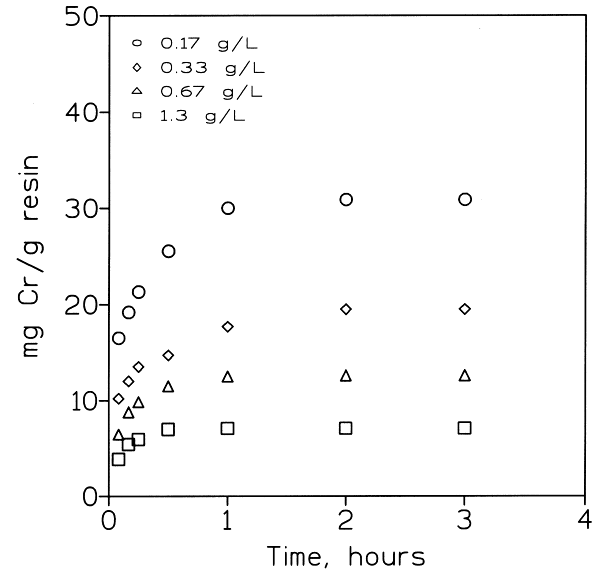

Fig.3 Effect of resin concentration on loading kinetics. Initial solution: 10 mg/l Cr(VI) in 0.5 M HCl.

Continuous experiments: Results obtained from batch experiments were used to investigate the continuous adsorption of chromium(VI) by the resin Dowex 1×8 packed in columns.

Figure 4 shows the influence of inlet chromium concentration on the breakthrough curves (for the definitions of the terms Bed Volume (BV) and breakthrough in Fig.4 and Table 1 see the miniprint format). As could be expected, increasing the metal concentration reduces the breakthrough volume significantly, however the reduction is not proportional to that of chromium concentration: it seems that increasing the concentration makes the system more efficient. Moreover, with increasing metal concentration, the slope of the breakthrough curves increases indicating a better mass transfer in the column. The breakthrough capacities were determined as 8.5, 11.4, 22.7 and 27.3 mg Cr/g resin for initial chromium concentrations of 20, 40, 80 and 160 mg/l, respectively.

Table 1 Elution efficiency

Eluent solution	Flow rate	% Cr eluted	BV
HNO_3 50%	254 BV/h	51.3	254
HNO_3 conc	152 BV/h	72.9	38
HNO_3 conc	84.5 BV/h	70.6	21
Sulfurous acid conc	254 BV/h	52.6	203
Sulfurous acid conc	84.5 BV/h	76.1	169
Hydrazine sulfate 50g/l	84.5 BV/h	51.4	70
Hydrazine sulfate 50g/l	254 BV/h	>99%	127
Sodium sulfite 50g/l	254 BV/h	37.8%	254

Initial resin loading: 70 mg/g. Temperature: 20°C

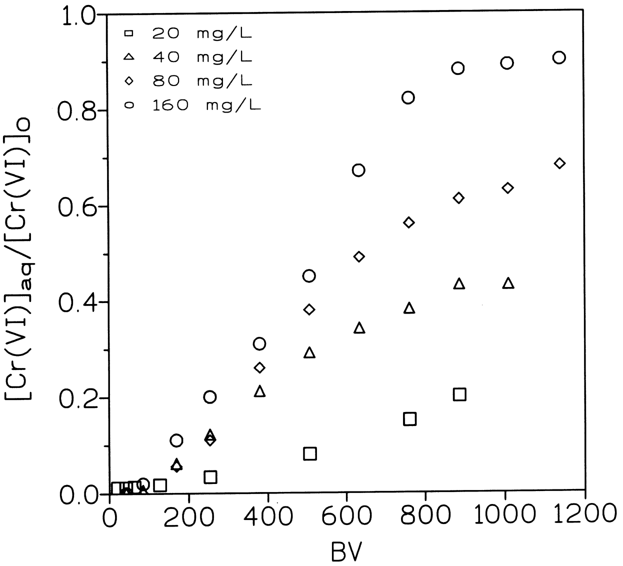

Fig.4 Influence of initial metal concentration on chromium(VI) adsorption breakthrough curves. Flow rate: 254 BV/hour. Initial solutions: chromium(VI) in 0.5 M HCl. Temperature: 20°C. Column: 0.5g resin.

Chromium elution from loaded resin: Strongly basic anion exchangers are difficult to elute. Several previous experiments had shown that only nitric acid at a concentration of more than 7 M was able to elute chromium(VI) from Dowex 1×8 among those solutions tested (acidic and alkaline reagents).[10] Thus, in the present investigation the elution of the metal from the resin was carried out with nitric acid solutions as well as with reducing agents like sulfurous acid, hydrazine sulfate and sodium sulfite solutions; in these lasts cases the objective was to elute the metal and reduced it to a less toxic form such as Cr(III). All the experiments were performed using a mini-column packed with 0.5g resin.

The results of the continuous experiments are presented in Table 1. As observed, hydrazine sulfate solution complete eluted chromium from the loaded resin at a given flow rate 3 ml/min (254 BV/h); however, concentrated nitric acid and sulfurous acid solutions also give a high percentage of metal elution under the conditions tested.

Further investigations were performed using the eluant (50 g/l hydrazine sulfate) flow rates of 1 and 3 ml/min (84.5 and 254 BV/hour, respectively). As a flow rate of 254 BV/h was applied, about 50% of chromium (initial resin load: 70 mg Cr(VI)/g resin) was eluted by 45 bed volume of eluant in near 12 min; if the eluant flow rate was reduced to 84.5 BV/h about 50% of chromium was eluted by 70 bed volume solution in an elution time of near 50 min. Only complete chromium elution is achieved using the higher flow rate and at the same time chromium(VI) is reduced to the (III) oxidation state.

From the results obtained, it is obvious that a higher flow rate needed a lower elution time and produced an eluate of lower concentration, whereas using lower flow rate produced an eluate of higher metal concentration and longer elution times.

On-line flow injection approach: The system was transferred to an on-line injection manifold system. Sample load and elution flow rates, sample and eluant volumes and micro-columns dimension were considered to be important factors in the design of the on-line ion-exchange FI system.[14] Micro-columns ranging from 0.2 to 0.5 cm (internal diameter) and from 20 to 50 mm in length were tested. The dimensional characteristics of the columns will be expressed in aspect ratios (ratio of the length to the internal diameter).[15]

Thinner and longer micro-columns with higher aspect ratios were found to yield larger breakthrough capacities and taller elution peaks. However, a higher back-pressure resulted in a deterioration of stability. With micro-columns presenting similar aspect ratios, those with a smaller volume produced higher elution peaks than larger volumes (provided that the exchange capacity was enough to the quantitatively retention of chromium).

Optimisation of the micro-columns dimensions was carried out, the performance of micro-columns with aspect ratios of 4 to 25 was studied. They were all packed with the resin and loaded with 2 ml of a 50 μg/ml Cr(VI) solution in a 0.5 M HCl medium, and eluted with 2 ml of the eluant (concentrated HNO_3 or hydrazine sulfate (50 g/l). The relative signals were estimated agaist Cr(VI) solutions in 1% v/v nitric acid. Good recoveries (exceeding 95%) and higher elution peaks were obtained for columns with small volumes (about 150 μl) and with aspect ratio value of near 20.

Concerning the sample flow rate it was proved that at low sample flow rate a large breakthrough capacity can be obtained. The residence time is inversely proportional to the sample flow rate. A sample flow rate of 0.9 ml/min was employed in order to obtain a complete retention of chromium(VI). In contrast to the loaded sample flow rate, the eluent flow rate does not significantly affect the elution process. Comparable elution signals were obtained for elution flow rates of 1.5 to 3.0 ml/min with the same column capacity. A careful evaluation of these parameters led to the conclusion that a good compromise between sensitivity and accuracy was a micro-column of 0.2 cm (internal diameter) and 40 mm total length, used with a 3.0 ml/min elution rate. With these operating conditions, quantitative recoveries of Cr(VI) (higher than 97%) were obtained using an on-line FI manifold system.

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References cited in this synopsis

1 S.Beszedits, in: *Chromium in the Natural and Human Environment*, J.O.Nrigau and E.Nieboer (eds), J.Wiley & Sons, New York, 1988.
2 M.W.Horn, B.G.Fraser, M.D.Pritzker and R.L.Legge, *Sep. Sci. Technol.*, 1994, **29**, 535.
3 T.-C.Huang, C.-C.Huang and D.-H.Chen, *Solvent Extr. Ion Exch.*, 1997, **15**, 837.
4 A.M.Sastre, A.Kumar, J.P.Shukla and R.K.Singh, *Sep. Purif. Meth.*, 1998, **27**, 213.
5 A.Alonso, A.Urtiaga, A.Irabien and I.Ortiz, *Chem. Eng. Sci.*, 1994, **49**, 901.
6 A.I.Alonso and C.Pentelides, *J. Membr. Sci.*, 1996, **110**, 151.
7 F.J.Alguacil, A.G.Coedo and M.T.Dorado, *Hydrometallurgy*, 2000, **57**, 51.
8 L.L.Tavlarides, J.H.Bae and C.K.Lee, *Sep. Sci. Technol.*, 1987, **22**, 581.

9 M.Iglesias, E.Anticó and V.Salvadó, *Anal. Chim. Acta*, 1999, **381**, 61.

10 A.G.Coedo, T.Dorado, I.Padilla and F.J.Alguacil, *J. Anal. At. Spectrom.*, 2000, **15**, 1564.

11 W.T.Yen and T.M.Sun, in: Proc. of the *XX International Mineral Processing Congress*, Vol.4, H.Hoberg and H. von Blottnitz (eds), GDMB, Clausthal-Zellerfeld, 1997.

12 E.Guibal, C.Milot and J.M.Tobin, *Ind. Eng. Chem. Res.*, 1998, **37**, 1454.

13 D.Barba, F.Beolchini and F.Veglio, *Hydrometallurgy*, 2000, **59**, 89.

14 Z.Fang and B.Welz, *J. Anal. At. Spectrom.*, 1989, **4**, 543.

15 M.A.Marshall and H.A.Mottola, *Anal. Chem.*, 1985, **57**, 729.