

The removal of toxic metals from liquid effluents by ion exchange resins.

Part I: Chromium(VI)/Sulphate/Dowex 1×8(*)

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Abstract

The removal of chromium(VI) from sulphuric acid solutions using the Dowex 1×8 resin has been investigated. The influence of several variables such as the stirring speed, temperature, the sulphuric acid and metal concentrations in the aqueous phase and the variation of the amount of resin added has been studied. Various aqueous solutions were used for the elution of the metal. Although concentrated nitric acid elutes chromium, this can be best accomplished using hydrazine sulphate 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. Moreover, an analytical application of the system in the determination of Cr(VI) presents in the leachate of an EAF dust was investigated by transferring the methodology to an on-line flow injection system.

Keywords

Liquid effluents. Removal. Chromium(VI). Sulphate. Dowex 1×8.

La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte I: cromo(VI)/sulfato/Dowex 1×8

Resumen

Se estudia la eliminación de cromo(VI) presente en disoluciones de ácido sulfúrico mediante la resina Dowex 1×8. Las variables experimentales estudiadas fueron: velocidad de agitación, temperatura, las concentraciones de metal y ácido sulfúrico en el medio acuoso y la cantidad de resina añadida. Se utilizaron diversas disoluciones acuosas para eluir al metal. Aunque el ácido nítrico se puede utilizar como eluyente, la operación de elución parece ser más eficiente cuando se emplean disoluciones de sulfato de hidracina que, al mismo tiempo, reduce el cromo(VI) a cromo(III). Los resultados obtenidos en los ensayos en discontinuo se han experimentado en sistemas en continuo, utilizando mini-columnas. Por último, se ha aplicado el sistema a la determinación analítica del cromo(VI) presente en los lixiviados de un polvo de horno de arco eléctrico, transfiriendo la tecnología a un sistema on-line con inyección de flujo.

Palabras clave

Efluentes líquidos. Eliminación. Cromo(VI). Sulfato. Dowex 1×8.

1. INTRODUCTION

Chromium, being one of the top-ten most abundant metals in the Earth's crust, is widely used in the industries (i.e. steel and leather processing) but it is also an environmental pollutant^[1]; specially hexavalent chromium species are known to be carcinogenic agents for various organisms.

Various processing alternatives had been suggested (and used) for the treatment of

chromium(VI) species-bearing liquid effluents including ion exchange technology. Ion exchange is a chemical treatment process used to remove dissolved ionic (anionic and/or cationic) species from contaminated aqueous streams^[2]. Common applications of ion exchange for the treatment of hazardous wastes are the removal and/or recovery of metal ions and cyanide from industrial rinse waters and wastewaters, treatment of contaminated ground water, and treatment of landfill leachate.

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On the other hand, some of the most often encountered analytical problems are associated with both the interferences of the sample media and the low concentration levels. For analytical purposes, solid-liquid (i.e. ion exchange resins) separation can be applied as a preconcentration technique^[3].

In the present work the adsorption and elution of chromium(VI) from sulphuric acid solutions using the anionic exchange resin Dowex 1×8 are investigated. 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 to investigate a possible analytical application of the system in the determination of chromium(VI) in leachates obtained by dissolution of solid wastes such as electric arc furnace flue dusts.

2. EXPERIMENTAL

The ion exchange resin Dowex 1×8 (Fluka) was used to adsorb chromium(VI) from sulphuric acid solutions. Dowex 1×8 is a strongly basic anion exchanger containing an active group of trimethylammonium (Cl⁻ form). It was used for chromium adsorption without pre-treatment. The micrograph of the resin obtained by scanning electron microscopy (Fig. 1) shows an uniform

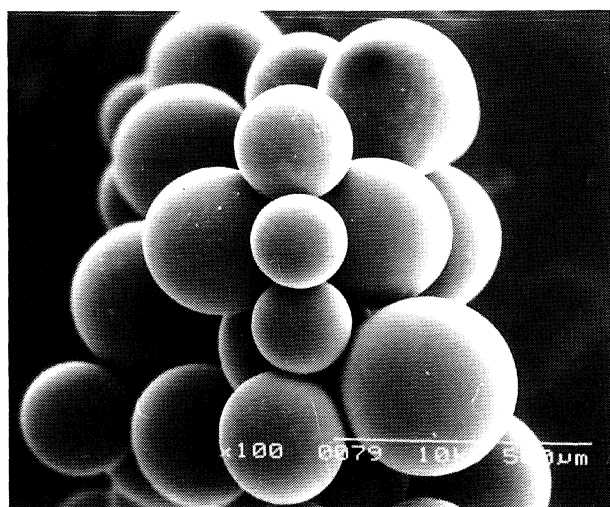


Figure 1. SEM of the Dowex 1×8 resin beads.

Figura 1. Micrografía de la resina Dowex 1×8.

structure; as it is also shown, the lack of surface porosity, makes Dowex 1×8 a gel type resin; surface area is large as particle size is heterogeneous and relatively small (150-300 μm). Aqueous Cr(VI) stock solution was prepared from solid K₂Cr₂O₇ (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 and temperature. The remaining metal in the aqueous phase was determined by AAS 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 feed with the corresponding aqueous solutions. Samples were regularly collected and analysed.

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.

3. RESULTS AND DISCUSSION

3.1. Adsorption

The effect of stirring was studied. 0.05 g of resin was used to adsorb chromium from a solution of 0.01 g/l Cr(VI) in 0.5M sulphuric acid (300 ml) with agitation speeds in the 500-1100 min⁻¹ range and 20 °C. Results obtained indicated that chromium(VI) adsorption was not dependent on agitation speed within the present range. Probably the adsorption process can be attributed to an interparticle or mixed diffusion-controlled process^[4]. A speed of 750 min⁻¹ was chosen as standard testing conditions.

The kinetics of resin loading were investigated at 20, 35 and 50 °C using 0.05 g resin in a solution of 0.01 g/l Cr(VI) (300 ml) with 750 min⁻¹. Results shows that the increase of solution temperature retarded the adsorption kinetics. Hence, 20 °C was used as the standard testing condition.

Several experiments have been conducted to study the effect of initial sulphuric acid concentration in the aqueous solution on chromium(VI) adsorption by the resin. Figure 2 shows that the decrease of the acidic concentration accelerated the adsorption kinetics up to 0.12M H_2SO_4 , however, the percentage of chromium(VI) adsorption increases with the decrease in the H_2SO_4 concentration up to 0.06M of acid.

To study the effect of initial chromium(VI) concentration, experiments were conducted by adding 0.2 g resin to a 300 ml solution containing 0.01-0.04 g/l Cr(VI) in 0.5 M H_2SO_4 at 20 °C and agitation speed of 750 min^{-1} . Figure 3 shows that the adsorption rate was fast at the initial stage: more than 50 % of chromium(VI) was adsorbed in near 15 min with the resin loading approaching a plateau after 45 min contact with the solution. More than 96 % of chromium(VI) was adsorbed by the resin within 1 h of contact for all initial chromium(VI) concentrations. The resin loading ranged from 6.8 mg Cr(VI)/ g resin to 18.9 mg Cr(VI)/ g resin depending on the initial metal concentration.

The influence of resin concentration was next investigated. 0.05-0.8 g resin were used to contact 300 mL solution containing 0.01 g/l Cr(VI) in 0.5M H_2SO_4 at 20 °C at an agitation speed of 750 min^{-1} . Figure 4 shows that the resin of 0.8 g

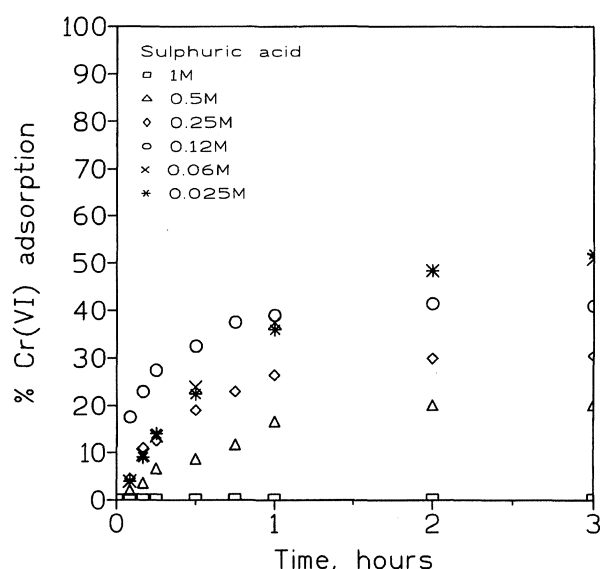


Figure 2. Influence of sulphuric acid concentration on Cr(VI) adsorption. Aqueous phase (300 mL): 0.01 g/l Cr(VI) and sulphuric acid. Resin: 0.05 g. Temperature: 20 °C.

Figura 2. Influencia de la concentración de ácido sulfúrico sobre la adsorción de Cr(VI). Fase acuosa: 0,01 g/l Cr(VI) y ácido sulfúrico. Resina: 0,05 g. Temperatura: 20 °C.

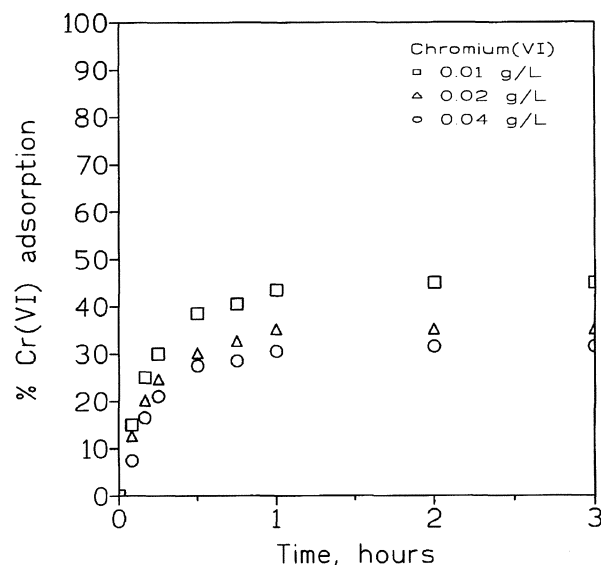


Figure 3. Effect of initial chromium(VI) concentration on metal adsorption.

Figura 3. Efecto de la concentración inicial de cromo(VI) sobre la adsorción del metal.

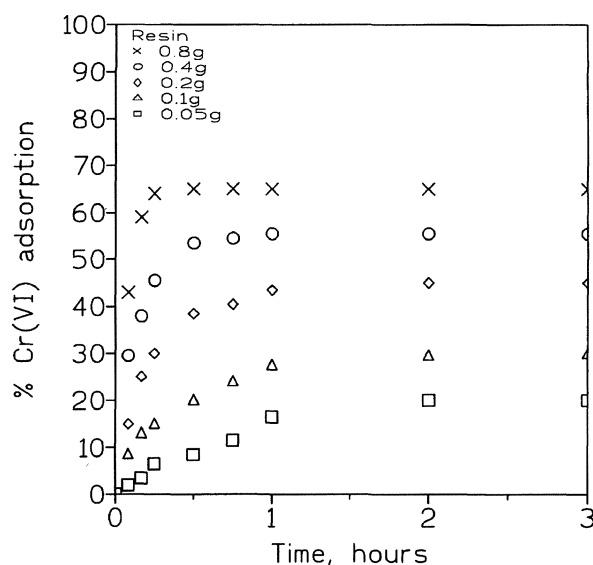


Figure 4. Effect of resin concentration on chromium(VI) adsorption..

Figura 4. Efecto de la concentración de resina sobre la adsorción de cromo(VI).

adsorbed near 90 % of chromium(VI) from the solution in 10 min with a resin loading of 2.4 mg Cr(VI)/ g resin. The metal adsorption from 0.05 g resin was much slower: 45 % and 90 % of Cr(VI) was recovered respectively in near 30 min and 1 h with a resin loading of 5.4 mg Cr(VI)/g resin and 10.8 mg Cr(VI)/g resin. It is obvious that

depending upon the volume of effluent to be treated and/or the inlet chromium(VI) concentration a minimum resin concentration must be selected to reach a fast and adequate chromium(VI) removal in the aqueous stream.

The adsorption isotherm of Dowex 1×8 was determined at 20 °C in a 300 mL solution containing an initial concentration of 0.01 g/l Cr(VI) and 0.5M H₂SO₄ for 3h. Resin of 0.05-0.8 g were used. The results show that the relationship between the resin loading and the metal equilibrium concentration was described by the Freundlich equation (with $r^2 = 0.988$) as follows^[5 and 6]:

$$[Cr(VI)]_r = k [Cr(VI)]_{aq}^n \quad (1)$$

where, $[Cr(VI)]_r$ is the resin loading in mg Cr(VI)/g resin, $[Cr(VI)]_{aq}$ is the metal equilibrium concentration in mg/l, and n and k are constants. The experimental values of n and k for the chromium(VI) adsorbed on Dowex 1×8 were 1.89 and 0.24, respectively.

To characterize the Dowex 1×8 resin under dynamic conditions, the breakthrough capacity of Cr(VI) was determined. The breakthrough capacity, being defined as the amount of metal ion that is retained per unit mass of resin before being detected in the outlet of the column, has in this case been operationally defined by the effluent concentration being equal to the 5 % of the inlet concentration.

Breakthrough curves obtained for different concentrations of Cr(VI) with 0.5g of resin at a flow rate of 3 ml/min and 0.025M H₂SO₄ are shown in figure 5. From this plot it can be seen that a lower chromium(VI) concentration reduces the breakthrough capacity of the metal; on the other hand, the breakthrough point ($[Cr(VI)]_t/[Cr(VI)]_0 = 0.05$) is reached at higher BV (Bed Volume) values as the metal concentration in the inlet solution is decreased. Breakthrough capacities were estimated as 38, 40 and 45 mg Cr(VI)/g resin for initial Cr(VI) concentrations of 0.16, 0.32 and 0.64 g/l, respectively.

3.2. Elution

Strongly basic anion exchangers are difficult to be eluted. Several previous experiments had shown that only nitric acid at a concentration of more than 7 M was able to elute chromium(VI) from

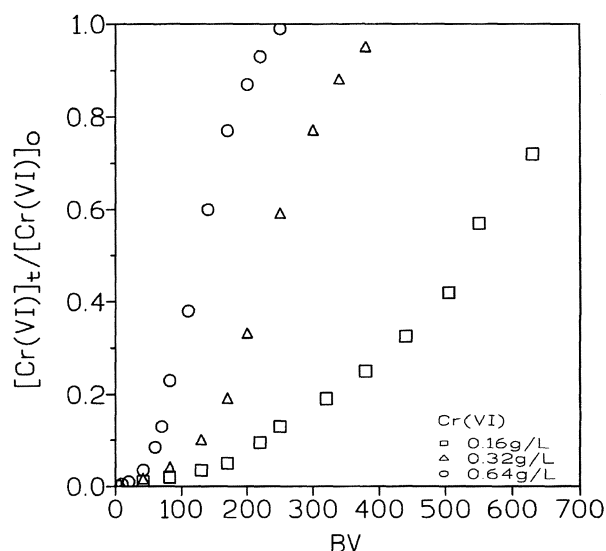


Figure 5. Influence of initial metal concentration on chromium(VI) adsorption breakthrough curves. Temperature: 20 °C.

Figura 5. Influencia de la concentración inicial de metal en las curvas de ruptura. Temperatura: 20 °C.

Dowex 1×8 among those solutions tested (acidic and alkaline reagents). 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 sulphurous acid, hydrazine sulphate and sodium sulphite solutions; in these last 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 I. As observed, hydrazine sulphate solution complete eluted chromium from

Table I. Elution efficiency

Tabla I. Eficiencia en la elución

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
Sulphurous acid conc	254 BV/h	52.6	203
Sulphurous acid conc	84.5 BV/h	76.1	169
Hydrazine sulphate 50g/l	84.5 BV/h	51.4	70
Hydrazine sulphate 50g/l	254 BV/h	>99%	127
Sodium sulphite 50g/l	254 BV/h	37.8%	254

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

the loaded resin at a given flow rate 3 ml/min (254 BV/h); however, concentrated nitric acid and sulphurous acid solutions also give a high percentage of metal elution under the conditions tested.

Figure 6 shows the elution results using the eluant (50 g/l hydrazine sulphate) flow rates of 1 and 3 ml/min (84.5 and 254 BV/h, respectively). As a flow rate of 254 BV/h was applied, about 50 % of chromium was eluted by 45 bed volume of eluant in about 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 about 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.

For the eluates obtained from the experiments described above, the chromium concentration in the solution was considered against the elution bed volume. Eluting at 254 BV/h, the highest eluate concentration was 0.65 g/l Cr(III) (8.45 BV) with an average of 0.41 g/l Cr. As the flow rate of eluate was decreased to 84.5 BV/h, the highest concentration of eluate was 2.8 g/l chromium (0.7 BV) with an average of 0.71 g/l. 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.

3.3. Analytical application

Some solid wastes may contain a relatively high level of toxic metals (i.e. Cr(VI)) which classifies them as hazardous wastes. The disposal of such materials in landfill sites is regarded as an environmental hazard due to toxic metals that may be leached into drinking waters supplies^[7]. Thus, tests were conducted to investigate a possible analytical application of the Cr(VI)/Dowex 1×8 system in the determination of the Cr(VI) content in a solid waste (i.e. an electric arc furnace flue dust). This type of solid waste can also be subjected to an accidental or deliberated leaching process. The Cr(VI)/Dowex 1×8 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^[8]. 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)^[9].

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 the 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).

According with literature results^[10], optimisation of the micro-columns dimensions using synthetic solutions was carried out. The Cr(VI) content in the solutions, simulated actual Cr(VI) concentrations found in solutions obtained from the dissolution of an EAF dust.

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 (g/ml Cr(VI) solution in a 0.16M H₂SO₄ medium, and eluted with 2 mL of the eluant (concentrated HNO₃ or hydrazine sulphate (50 g/l). The relative signals were estimated against Cr(VI) solutions in 1 % v/v nitric acid. Good recoveries (exceeding 95%) and higher elution peaks were obtained for

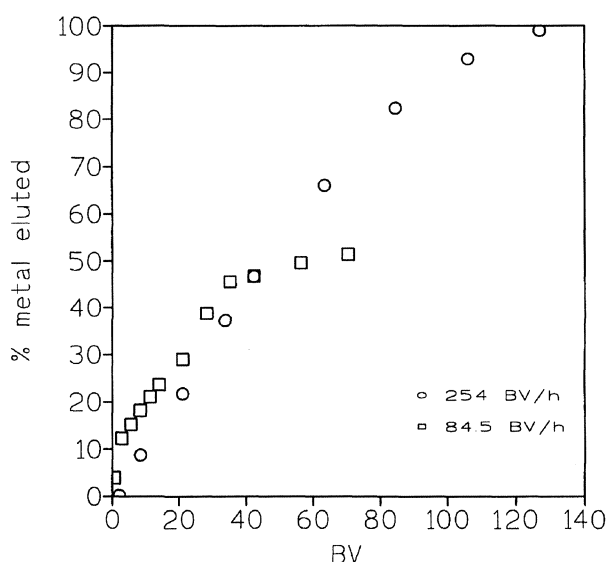


Figure 6. Effect of flow rate on chromium elution from resin. Initial resin loading: 70 mg Cr(VI)/ g resin. Eluent solution: 50 g/l Hydrazine sulphate. Temperature: 20 °C.

Figura 6. Efecto del flujo sobre la elución del cromo. Carga en la resina: 70 mg Cr(VI)/ g resina. Disolución eluyente: 50 g/l sulfato de hidracina. Temperatura: 20 °C.

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.

4. CONCLUSIONS

Chromium(VI) adsorption from sulphuric acid solutions on Dowex 1×8 ion exchange resin is fast and the resin having a reasonable loading capacity. The adsorption isotherm was described by the Freundlich equation. Under the conditions of 0.2 g resin and 750 min^{-1} stirring speed, more than 96 % of chromium(VI) could be recovered by the resin in near 1 h contact with a solution of 0.01 g/l Cr(VI) at 20 °C. If the initial amount of resin is increased to 0.4 g, the chromium recovery was higher than 95 % in less than 30 min. Adsorption kinetics decreased as the temperature was increased (from 20 °C). Breakthrough capacities decrease as the concentration of chromium in the inlet solution decreases. The loaded resin could be readily eluted using nitric acid or hydrazine sulphate solutions at 20 °C; however, from an

environmental point of view this last option seems to be more attractive since at the same time chromium(VI) is reduced to the less toxic chromium(III). The adsorption system was successfully transferred to the analytical determination of the Cr(VI) content in an EAF dust, under the proper operating conditions, quantitative recoveries of Cr(VI) (exceeding 97 %) were obtained using an on-line FI manifold system.

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