

The removal of toxic metals from liquid effluents by ion exchange resins. Part IV: Chromium(III)/H⁺/Lewatit SP112

Francisco José Alguacil✉

Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, España
✉Corresponding author: fjalgua@cenim.csic.es

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ABSTRACT: This investigation presented results on the removal of chromium(III), from aqueous solution in the 0-5 pH range, using Lewatit SP112 cationic exchange resin. Several aspects affecting the ion exchange process were evaluated, including: the influence of the stirring speed, temperature, pH of the solution, resin dosage and aqueous ionic strength. The selectivity of the system was tested against the presence of other metals in the aqueous solution, whereas the removal of chromium(III) from solutions was compared with results obtained using multiwalled carbon nanotubes as adsorbents. From the batch experimental data, best fit of the results is obtained with the Langmuir model, whereas the ion exchange process is best explained by the pseudo-second order model, moreover, experimental data responded well to the film-diffusion controlled model. Elution of the chromium(III) loaded into the resin is well accomplished by the use of sodium hydroxide solutions.

KEYWORDS: Chromium(III); Lewatit SP112; Liquid effluents; Removal

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RESUMEN: *La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte IV: cromo(III)/H⁺/Lewatit SP112.* En este trabajo se presentan los resultados obtenidos en la eliminación de cromo(III) de disoluciones acuosas (pH 0-5) mediante la resina de intercambio catiónico Lewatit SP112. Se han investigado algunas variables que pueden afectar al sistema: influencia de la agitación, temperatura, pH y fuerza iónica del medio acuoso y cantidad de resina; también se ha investigado acerca de la selectividad del sistema cuando otros metales están presentes en el medio acuoso, comparándose los resultados de la eliminación del cromo(III) usando la resina con los resultados obtenidos cuando se emplea otro adsorbente como son los nanotubos de carbono de pared múltiple. Los resultados experimentales indican que la carga del cromo(III) en la resina responde mejor al modelo de Langmuir, mientras que los modelos cinéticos indican que la carga del metal en la resina responde al modelo de pseudo-segundo orden y difusión en la capa límite. La elución del cromo(III) se realiza con disoluciones de hidróxido sódico.

PALABRAS CLAVE: Cromo(III); Efluentes líquidos; Eliminación; Lewatit SP112

ORCID ID: Francisco José Alguacil (<http://orcid.org/0000-0002-0247-3384>)

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1. INTRODUCTION

Though chromium(III) does not present the severe toxicological aspects of chromium(VI), it is considered a hazardous element due to its own and also to the possibility of its oxidation to the (VI) oxidation state, and thus, changing dramatically the labelling of a given liquid solution or effluent. Thus, the elimination of chromium(III) is a real challenge and necessity when it is present in the liquid waste. In practice, the limiting values for chromium concentrations in liquids streams changed by countries and from one source to another i.e., permissible limits for chromium are 0.1 mg.L^{-1} in industrial wastewaters and 0.05 mg.L^{-1} for potable waters (Alguacil *et al.*, 2013), whereas in the USA, the standard for drinking waters is 0.1 mg.L^{-1} total chromium (USEPA, 2016) and 0.5 mg.L^{-1} chromium in estuary and harbour basin water.

Based in the above, and following the series of articles published by the author about the use of ion exchange technology in the removal of toxic metals (Alguacil *et al.*, 2002; Alguacil, 2002; Alguacil, 2003), the present work investigates about the use of Lewatit SP112 ion exchange resin on the removal of chromium(III) from aqueous solutions, several variables which may affect to the ion exchange process were investigated, whereas various models were tested to fit the various aspect of the exchange process.

2. EXPERIMENTAL

Lewatit SP112 (Fluka) having the characteristics shown in Table 1 were used to test the removal of chromium(III) from solutions. Other chemical used in the investigation were of AR grade, whereas the experimental procedure used here was the same as described in previous works (Alguacil, 2002; Alguacil *et al.*, 2002; Alguacil, 2003). The multi-walled carbon nanotubes presented the characteristics described elsewhere (Alguacil *et al.*, 2016).

All the loading experiments were carried out at 1000 rpm and 20°C except when these variables were investigated.

Metals in solution were analysed by AAS spectrometry, whereas metal load in the resin was calculated by the mass balance.

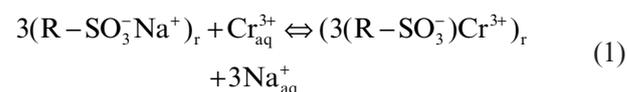
TABLE 1. Characteristics of Lewatit SP112 resin

Active group	Sulfonic in Na^+ form
Matrix	Crosslinked polystyrene-DVB
Pore size	Macroporous
Particle form and size	Spheres, 0.68 mm
Density	1.27 g.mL^{-1}

3. RESULTS AND DISCUSSION

3.1. Metal loading onto the resin

Being Lewatit SP112 a cationic exchanger, the reaction which describes the removal of chromium(III) from the solutions in the 0–5 pH range is:



where R is the non-reactive part of the resin, and r and aq represented the resin and the aqueous solution, respectively.

The influence of the stirring speed of the aqueous solution was first investigated in order to ensure a maximum in metal loading onto the resin, thus an aqueous solution containing 0.01 g.L^{-1} Cr(III) at pH 5 was put into contact with 0.5 g.L^{-1} of the resin, and the system was stirred at different stirring speeds. Results are shown in Fig. 1. The maximum in adsorption loading is reached at 1000 rpm. Consequently, the thickness of the aqueous phase reached a minimum and a maximum in chromium(III) loading is reached.

Temperature was other variable investigated, in this case, a resin dose of 0.5 g.L^{-1} and aqueous solution of 0.01 g.L^{-1} Cr(III) at pH 5 were used. The results, Table 2, show that the metal uptake increases as the temperature is increased, this same table gives the values of the chromium distribution coefficient, defined as:

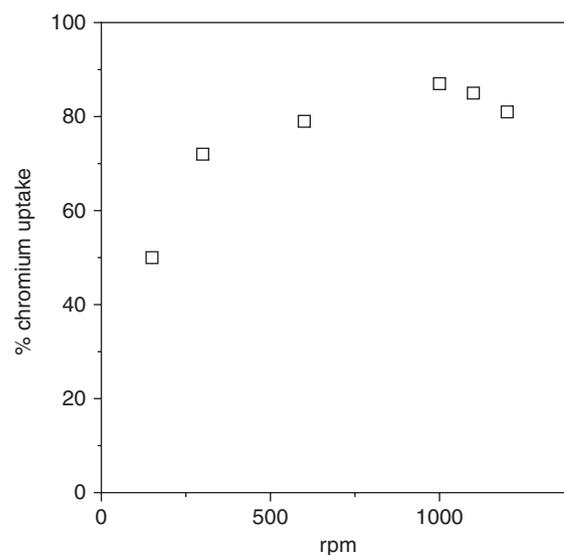


FIGURE 1. Chromium(III) loading onto the resin at various stirring speeds.

$$D = \frac{[Cr]_r}{[Cr]_{aq}} \quad (2)$$

where [Cr]_r and [Cr]_{aq} represented to the chromium concentrations at equilibrium in the resin and in the aqueous solution, respectively.

The thermodynamic values were estimated using conventional relationships, and indicated that the reaction is endothermic (ΔH° 14.5 kJ.mol⁻¹), whereas ΔS° and ΔG° are 35.4 J.mol⁻¹ K and 4.1 J.mol⁻¹, respectively. The positive entropy value indicates increases randomness at the solid-liquid interface during the ion exchange process, and the positive ΔG° value should be an indication that the exchange process is not spontaneous.

In order to investigate the role of the pH of the aqueous solution during the exchange of chromium(III), pH variation studies in the range 0-5 were carried out using 0.1 g.L⁻¹ of resin and an aqueous solution of 0.01 g.L⁻¹ Cr(III). As seen from Fig. 2, a maximum in metal load is reached at pH 3, though the difference between pH values of 3-5 is minimal, being chromium(III) loaded onto

the resin in a lesser extent as the pH reached highly acidic values.

The influence of the resin dosage on chromium loading was also investigated. Fig. 3 shows the variation in the metal exchanged or adsorbed onto the resin for resin doses of 1 to 0.125 g.L⁻¹. The metal adsorption increases with the resin dosage, though appreciable chromium adsorption was achieved even when 0.125 g.L⁻¹ of the resin were used to remove the metal from the aqueous solution. From the experiments, Table 3 presented data about metal uptake versus metal concentration in the solution at equilibrium, it was observed that the metal loaded onto the resin increased as the resin dosage decreased. These data were further used to obtain the metal loading isotherm and its best fit with the Langmuir or Freundlich models.

The effect of the aqueous ionic strength on chromium(III) loaded onto the resin was also investigated by the use of LiCl or HCl as source for the increase of the ionic strength. Results were summarized in Table 4, it can be seen that the increase of the aqueous ionic strength decreased the metal uptake, but the source of how this

TABLE 2. Influence of the temperature on metal uptake^a

T (°C)	[Cr] (mg.L ⁻¹)	[Cr] (mg.g ⁻¹)	D (L.g ⁻¹)	log D
20	0.4	19.2	48	1.68
40	0.3	19.4	65	1.81
60	0.2	19.6	98	1.99

^a Time: 5 h

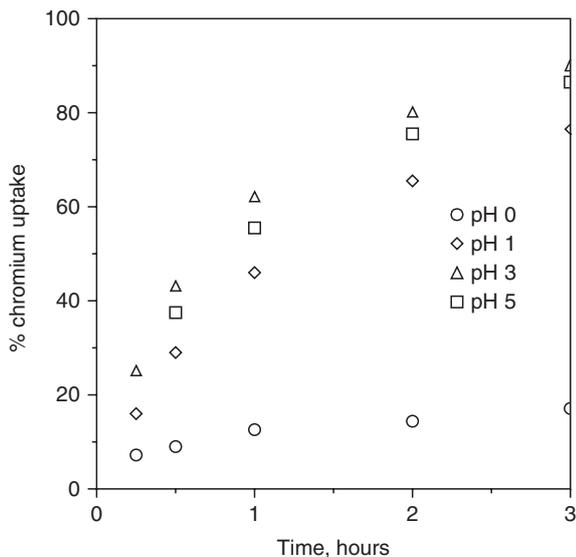


FIGURE 2. Influence of the pH on chromium(III) loading.

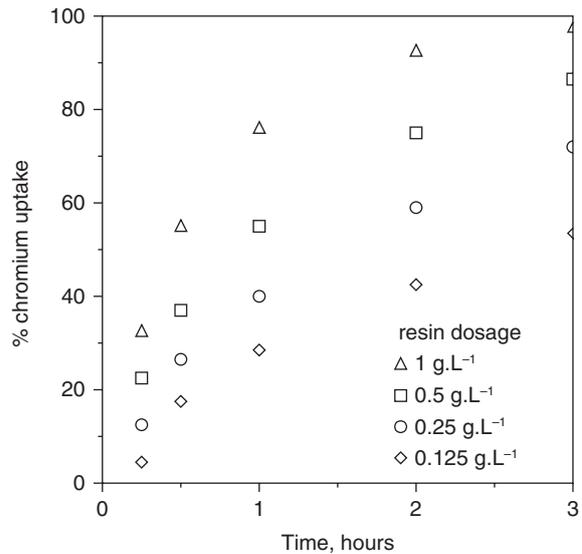


FIGURE 3. Influence of resin dosage on chromium(III).

TABLE 3. Metal uptake at equilibrium^a

Resin (g.L ⁻¹)	[Cr] (mg.L ⁻¹)	[Cr] (mg.g ⁻¹)
1	0.2	9.8
0.5	0.4	19.2
0.25	1.9	32.4
0.125	3.8	49.6

^a Time: 5 h

ionic strength was increased also influenced this load, because when HCl is presented in the aqueous solution the metal uptake was always lower than when LiCl was used as source for the ionic strength, probably by a competence between the protons and chromium(III) to exchange with the sodium ion of the resin.

The selectivity of the system was tested against the presence of other metals in the aqueous solution and in form of binary solutions. It should be noted here that chromium(VI) is not adsorbed or exchanged within the resin, thus Lewatit SP112 can be used for the quantitative separation of chromium(III) from mixed chromium(III)-chromium(VI) solutions. Results obtained from these series of tests are shown in Table 5 in the form of the metal distribution coefficient, see Eq. (2), at an elapsed time (3 h) and at equilibrium (5 h). In this same Table, the values of the separation factor β are given:

Table 4. Influence of the aqueous ionic strength on chromium adsorption

I, M	Source	Adsorption ^a (%)
0		86.9
0.25	LiCl	82.1
	HCl	78.0
0.5	LiCl	71.3
	HCl	53.8
0.75	LiCl	50.0
	HCl	39.2
1	LiCl	28.1
	HCl	17.1

^a Time: 3 h

$$\beta = \frac{D_{Cr}}{D_M} \quad (3)$$

It can be seen, that the separation of chromium from the other metals, $\beta > 1$, is favoured in the non-equilibrium conditions (3 h), because at the equilibrium (5 h), practically in all the cases the value of β decreases, even nickel is loaded onto the resin preferably to chromium(III) ($\beta < 1$).

As mentioned in the Abstract section, the performance of Lewatit SP112 was compared with results obtained in the removal of chromium(III) by multi-walled carbon nanotubes.

These results showed that with the carbon nanotubes a mere 5% of the metal is adsorbed onto the nanotubes, this result compares pretty bad with the 96% obtained with the resin. In the above experiments, the aqueous solution was 0.01 g.L⁻¹ Cr(III) at pH 5, whereas the resin or carbon nanotubes dosages were of 0.5 g.L⁻¹ and time 5 h.

The adsorption data were used to examine their fit to the Langmuir or Freundlich models (Alguacil *et al.*, 2016). The results of these tests show that the adsorption is best fit to the Langmuir model (R^2 : 0.976):

$$\frac{1}{[Cr]_{r,e}} = \frac{1}{Q_0} + \frac{1}{bQ_0} \frac{1}{[Cr]_{aq,e}} \quad (4)$$

with Q_0 58.8 mg.g⁻¹ and b 1.1 L.mg⁻¹. In the above equation, $[Cr]_{r,e}$ and $[Cr]_{aq,e}$ represented the chromium concentrations at equilibrium in the resin and in the aqueous solution, respectively, Q_0 represented the maximum adsorption capacity as estimated by the model, whereas b is a Langmuir constant.

TABLE 5. Metals uptake by the resin from binary solutions

Metal couple	^a D (L.g ⁻¹)	^a $\beta_{Cr(III)-Metal}$	^b D (L.g ⁻¹)	^b $\beta_{Cr(III)-Metal}$
Cr(III)	9	3.3	13.4	1.9
In(III)	2.7		7.1	
Cr(III)	7.1	1.1	10.2	0.9
Ni(II)	6.7		10.9	
Cr(III)	9	1.1	13.4	1.1
Mn(II)	8		12.5	
Cr(III)	9	1.2	13.4	1.1
Co(II)	7.3		12.7	
Cr(III)	9	1.4	13.4	1.1
Cu(II)	6.3		12.2	
Cr(III)	9	2.3	13.4	2.3
Fe(III)	4		5.8	

Aqueous solutions: Cr(III)-Metal in a 1:1 molar concentrations ratio, pH 5, except in the case of the mixture Cr(III)-Fe(III) in which the pH was 1. Resin dosage: 0.25 g.L⁻¹. Time: a) 3 h and b) 5 h

Adsorption or exchange kinetics was also evaluated. The pseudo-first and pseudo-second order rate equations (Alguacil *et al.*, 2016) were used to estimate their fit to the experimental data. Numerical results showed that the kinetics is best explained within the pseudo-second order model ($R^2 > 0.997$):

$$\frac{t}{[Cr]_{r,t}} = \frac{1}{k_2 [Cr]_{r,e}^2} + \frac{t}{[Cr]_{r,e}} \quad (5)$$

with k_2 (rate constant) in the 0.003–0.006 $\text{gmg}^{-1} \text{min}^{-1}$ range for resin doses of 1 to 0.125 g.L^{-1} . $[Cr]_{r,t}$ represented to the chromium concentration in the resin at an elapsed time, and $[Cr]_{r,e}$ is the chromium concentration in the resin at equilibrium.

Furthermore, the mechanism from which chromium(III) is loaded onto the resin was evaluated using the relationships described elsewhere (Alguacil *et al.*, 2016). Results of the experimental data fitting to the models, showed that in the 1–5 pH range, the rate law governing (best fitting) the chromium exchange within the resin is a liquid-solid phase reaction which includes diffusion of chromium(III) ion from the aqueous phase to the resin surface, and described by:

$$\ln(1 - F) = -kt \quad (6)$$

with rate constant k in the near 0.013 min^{-1} range (pH values 1-5) and $R^2 > 0.998$. In the above equation, the fractional attainment to the equilibrium, F , was calculated by the next relationship:

$$F = \frac{[Cr]_{r,t}}{[Cr]_{r,e}} \quad (7)$$

where $[Cr]_{r,t}$ and $[Cr]_{r,e}$ represented the chromium concentrations in the resin at time t and at equilibrium, respectively.

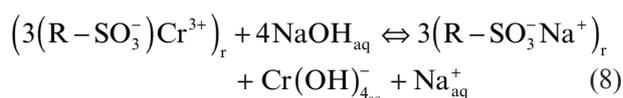
3.2. Metal elution from the loaded resin

Chromium(III) is best eluted from these types of resins when alkaline solutions were used as eluants (Alguacil *et al.*, 2012), thus experiments were carried out using NaOH solutions (25 mL) to study the effect of their concentration on metal elution (resin loaded with 17 mg Cr/g resin). Table 6 showed the results obtained from these set of experiments. It can be seen that the increase of the NaOH concentration increased the percentage of chromium(III) eluted from the loaded resin with a concentration factor of six times with respect to the chromium(III) concentration of the initial aqueous solution (0.01 g.L^{-1}), at the same time, the resin is regenerated to its Na^+ form:

TABLE 6. Chromium elution using NaOH solutions

NaOH (M)	Cr eluted (%)
0.1	9.2
0.5	91.5
1	91.3

Time: 1 h; Temperature: 20 °C



The meaning of R, r, and aq is the same as described previously (Eq. (1)).

4. CONCLUSIONS

- Lewatit SP112 resin can be used to remove chromium(III) from liquid wastes, though its selectivity against the presence of other elements, not chromium(VI), can be engaged under the given experimental conditions. The chromium(III) uptake is dependent of the pH of the solution, best at slightly acidic solutions or near neutral conditions, the temperature, the exchange reaction is endothermic, and the resin dosage. The exchange chromium(III)-sodium(I) is best related to the Langmuir isotherm, whereas the pseudo-second order kinetic model explained the exchange kinetics with k_2 values in the 0.003-0.006 $\text{g.mg}^{-1} \text{min}^{-1}$ range. The rate law governing the metal uptake is best described by the film-diffusion controlled process with rate constant about 0.013 min^{-1} . At near aqueous neutral condition, chromium adsorption or exchange is best with the resin than with the multiwalled carbon nanotubes tested in this work.

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