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The removal of chromium (III) from aqueous solution by ion exchange on Amberlite 200 resin: batch and continuous ion exchange modelling

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ABSTRACT

The use of ion exchange technology is studied for the removal of chromium (III) from acidic waste solution by Amberlite 200 resin. Batch and column experimental tests were conducted to provide data for theoretical models and verify the system performance of the removal process. Results of batch equilibrium tests indicated that Langmuir isotherm describes well the adsorption process, whereas experimental data also provide evidence that, under the present experimental conditions, the rate law which controlled chromium (III) adsorption by Amberlite 200 resin depends of the resin particle size; on the other hand, the theoretical model used in the present investigation was found to predict reasonably well the ion exchange breakthrough performance.

Keywords: Chromium (III); Amberlite 200; Ion exchange; Modelling; Wastewaters; Batch and continuous operations

1. Introduction

Metallurgical industries are constantly being forced by the more stringent regulatory and cost pressures to reduce the amount and environmental sensitivity of the various effluents they produce. Since heavy metals are considered as non-biodegradable toxic pollutants which may be released in the environment by the various industrial activities, they removal represents a necessary environmental challenge. In the case of liquid effluents, there are many methods available for the removal of these metals: chemical precipitation, coagulation, solvent extraction and membrane processes, and among them, adsorption and ion exchange processing have been merged as economical feasible alternatives.

Thus, ion exchange and adsorption are becoming popular methods that are being receiving much attention for the removal of metallic species from aqueous solutions [1–10]. Some of the potential advantages of ion exchange include the possible recovery of the metal and the possibility of working with no-clarified solutions, lower sludge volume produced and the meeting of strict discharge specifications, whereas certain lack of selectivity may be the main drawback of the technology.

Different industrial applications call for various forms of chromium. Such as chromite, ferrochromium, chromium metal, chromite refractory bricks, chromite foundry sands, chromic acid, and other chromium compounds, while the principal industrial applications of chromium and its compounds included non-ferrous and ferroalloys, refractories, chemicals (metal finishing and corrosion control, leather tanning and finishing, pigments, wood preservative, etc.).

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This element occurs in aqueous systems in both the trivalent form (Cr^{3+}) and the hexavalent form (acidic chromate $HCrO_4^-$ and dichromate $Cr_2O_7^{2-}$), and whereas Cr(VI) has long been recognized as a toxic substance to animal and plants, Cr(III) is considered to be less toxic, though its elimination from contaminated waters is also of a primarily necessity in industrialized countries due to the possibility of oxidation to the Cr(VI) state.

In the case of Cr(III), the legal discharge limit for the metal varies from 2 to 4 mg l^{-1} (in sewers) or less depending on the processing and country, whereas drinking water standards have been set at 0.05 mg l^{-1} total chromium [11,12].

For Cr(III)-bearing liquid effluents, the methods for treating this contaminated solutions fall within those mentioned above [13–21]; however, at low solute feed concentrations, the use of some of these methods lose their advantage and the use of a solid matrix for ion exchange of contaminants provides a feasible alternative, that is sorption in a solid support has properties nearly identical to those of the organic phase in liquid–liquid extraction or solvent-based membrane processes but with two main advantages, no mixing and settling requirements have to be fulfilled and no lost of organic phase through entrainment occurs.

The objective of the present study is to address the performance of Amberlite 200 ion exchange resin in the removal of Cr(III) from aqueous solution. Various parameters were studied, in both batch and continuous operational modes, to optimize conditions for effective removal of this metal ion from water containing it.

2. Experimental

Amberlite 200 (obtained from Fluka) is a macroporous cation exchange resin, which main characteristics are given in Table 1. All other chemicals used in the present work were of AR grade. Aqueous solutions were analysed for chromium by using a Perkin Elmer 1100B AAS.

Batch operation: equilibrium adsorption experiments were carried out by the use of a weighed amount of resin (1 g) which were contacted, under agitation rate of 850 min^{-1}, in a glass reactor with 200 ml aqueous solution containing chromium (III) nitrate at 25°C and for various times. Previous experiments had shown that within this stirring speed both the elimination of the bulk aqueous phase convection and the minimization of the thickness of the aqueous diffusion film are achieved. The residual Cr(III) concentrations in the aqueous solution after the desired treatment and time were measured by AAS. The metal uptake by the resin was calculated from the residual concentration of chromium in the aqueous phase. The fractional approach to equilibrium (F) was calculated by:

$$F = \frac{[\mathrm{Cr}]_0 - [\mathrm{Cr}]_t}{[\mathrm{Cr}]_0 - [\mathrm{Cr}]_\mathrm{e}} \quad (1)$$

where $[\mathrm{Cr}]_0$ is the initial solution concentration, $[\mathrm{Cr}]_t$ is the concentration at an elapsed time and $[\mathrm{Cr}]_\mathrm{e}$ is the chromium concentration in the aqueous solution at equilibrium. In the present investigation, it is considered that equilibrium is attained when chromium concentration in the aqueous solution, and thus, chromium loaded in the resin, is constant with the time.

Continuous operation: column trials were carried out with 1 g resin, which was loaded into the column with a nominal capacity of 5 ml and fitted with 20 μm polyethylene frit as bed support. Aqueous phases containing chromium (III) were passed downwards through the bed using a peristaltic pump. The effluent from the column was either directed to the fraction collector or to the waste. Samples were collected regularly and analysed (AAS) to monitor the chromium concentration leaving the column.

Batch and continuous elution tests were carried out in similar devices as described above.

Table 1
Characteristics of Amberlite IR-200 ion exchange resin

Polymer matrix	Styrene-DVB
Functional group	Sulfonic acid
Ionic form	H^+
Exchange capacity	4.4 meq g^{-1} (dry)
Operating temperature	120°C (maximum)
Effective size	0.45–0.60 mm

3. Results and discussion

3.1. Batch experiments

The influence of pH on the adsorption of Cr(III) by Amberlite 200 had been studied using an aqueous solution containing 0.3 g l^{-1} chromium, and the results obtained are presented in Table 2. As it can be expected from cationic exchange resins, it can be seen that metal uptake increases from pH 1 to 3 and then remained near

Table 2
Chromium (III) uptake as a function of the aqueous solution pH value

pH	mg Cr(III) g^{-1} resin
1	45.0
3	58.8
5	59.4

constant at higher pH values. This calls for a possible application of this resin in the removal of chromium (III) contained in rinse waters from stainless steel pickling, which generally presented pH values near three.

On the other hand, studying the influence of the variation of the temperature between 10°C and 40°C in the metal adsorption, from an aqueous solution containing 0.01 g l^{-1} Cr(III) at pH 3.0 ± 0.05, has shown that this variable has a negligible effect on chromium (III) uptake (averaging >1.9 mg Cr(III) g^{-1} resin for the above temperature range) by Amberlite 200 resin, though initial metal adsorption rate slow down as the temperature decreases.

The Langmuir and Freundlich models are two general isotherms commonly used to describe the equilibrium ion exchange relation between the solid and liquid phases; these models are represented respectively by:

$$[M]_r = \frac{ab[M]_e}{1+b[M]_e} \tag{2}$$

$$[M]_r = k[M]_e^n \tag{3}$$

where $[M]_r$ and $[M]_e$ are the equilibrium ion exchange capacity of the resin and the equilibrium metal concentration in the aqueous solution, respectively, and a, b, k and n are the constant isotherm parameters. The observed data of the equilibrium ion exchange tests are shown in Fig. 1. This figure also shows the model fit using the two isotherms. The model fit (Table 3) reveals that the Langmuir isotherm represents Amberlite 200 adsorption of Cr(III) better the Freundlich isotherm. The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. The isotherm parameters obtained by the model fit are listed in the same table, these isotherm parameters allow easy determination of the equilibrium ion exchange capacity of the ion exchange resin for different Cr(III) initial concentrations.

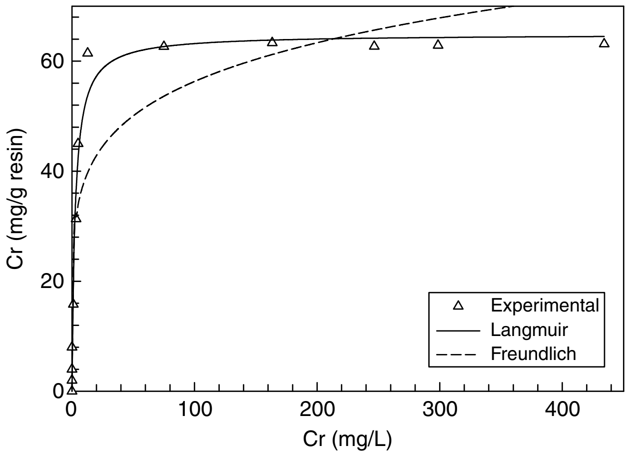

Fig. 1. Isotherm model fits of experimental equilibrium ion exchange data of Amberlite 200 at 25°C.

Table 3
Parameters of the Freundlich and Langmuir isotherms

	r^2	k (mg g_{resin}^{-1})	n	a (mg g_{resin}^{-1})	b (l mg^{-1})
Freundlich	0.870	25.7	0.17	–	–
Langmuir	0.981	–	–	64.9	0.38

k relates to sorption capacity, n to sorption intensity, a to adsorption capacity and b to energy of adsorption.

The rate law governing the adsorption of chromium (III) by Amberlite 200 had been determined by using various experimental conditions. Three possible adsorption mechanism had been evaluated if the adsorption of chromium (III) into the resin must be considered as a liquid-solid phase reaction which includes diffusion of chromium ions from the aqueous phase to the resin surface, the diffusion of ions within the resin and the chemical reaction between ions and resin functional groups. The rate equations for the above three cases are [22]:

(1) film-diffusion controlled process, the rate equation is:

$$\ln(1-F) = -kt \tag{4}$$

Being the adsorption or ion exchange process controlled by the diffusion of the metal ions through the liquid film surrounding the particle, and it depends on the solute concentration at a constant particle size.

(2) particle-diffusion controlled process, with the equation as:

$$\ln(1-F^2) = -kt \tag{5}$$

In which the model assumes constant diffusion through the solid particle pores, and (3) shrinking core model:

$$3-3(1-F)^{2/3}-2F = kt \tag{6}$$

In this case, the model assumes a sharp boundary that separates a completely reacted shell from an unreacted core.

In Eqs. (4)–(6), F is the fractional approach to equilibrium, whereas k is the corresponding rate constant. Results from the present investigation are shown in Table 4, and shows that the metal uptake by Amberlite 200 resin is best fitted by the shrinking core model at the higher resin particle size, whereas at the lower particle size chromium uptake is explained either by the

Table 4
The regression coefficients and rate constants for the tested adsorption mechanisms of chromium onto Amberlite 200 resin

Resin size	Equation	r^2	k (s^{-1})
495–981 μm	$\ln(1-F)=-kt$	0.982	1.8×10^{-5}
	$\ln(1-F^2)=-kt$	0.985	1.3×10^{-5}
	$3-3(1-F)^{2/3}-2F=kt$	0.994	3.3×10^{-6}
246–495 μm	$\ln(1-F)=-kt$	0.994	2.5×10^{-5}
	$\ln(1-F^2)=-kt$	0.992	2.2×10^{-5}
	$3-3(1-F)^{2/3}-2F=kt$	0.943	5.0×10^{-6}

Aqueous phase: 0.3 g l^{-1} Cr(III) at pH 3.0 ± 0.05. Temperature: 25°C.

film-diffusion controlled mechanism or by the particle-diffusion process.

3.2. Continuous experiments

Similarly to other unit operations, ion exchange is a process whose performance is affected by a number of operational parameters, including the equilibrium resin adsorption capacity and the mass transfer rate. Prediction of column performance usually involves the resolution of a set of nonlinear partial differential equations, though as an alternative, a macroscopic version, from the above, can be used for describing the behaviour of a column adsorber. In most instances, the equation which represented the macroscopic model is written as [23]:

$$\ln\frac{[M]_t}{[M]_0-[M]_t}=k\,[M]_0\left(t-\frac{[M]_e\,m}{[M]_0\,f}\right) \tag{7}$$

where $[M]_t$ is the solute concentration in the outlet solution at time t, $[M]_0$ is the inlet solute concentration, k is the rate constant of adsorption, $[M]_e$ is the equilibrium solid-phase (i.e., resin) concentration of sorbed solute, m the mass of adsorbent, f is the flow rate and t is the time. According to the above equation, the left-hand quantity is a linear function of time, and in fact, the above equation is essentially the same as the simplified logistic function that describes the biological or population growth and distribution:

$$\ln\frac{[M]_t}{[M]_0-[M]_t}=k(t-\tau) \tag{8}$$

Table 5
Parameters of Eq. (8)

Flow rate (cm^3 min^{-1})	Inlet concentration^a (g l^{-1})	k (min^{-1})	τ (min)
3	0.1	0.02	350.7
6	0.1	0.03	155.4
12	0.1	0.05	65.8
12	0.05	0.03	132.9

^{a}At pH 3.0 ± 0.05.

The two parameters in Eq. (8) can be readily estimated from the slope (k) and the intercept (τ) when plotting $\ln [M]_t/[M]_0-[M]_t$ versus time. The estimated parameters for Amberlite 200 adsorption of Cr(III) for different inlet metal concentrations and flow rates are listed in Table 5. Using the estimated parameters, the breakthrough curves for various inlet concentrations and flow rates could be predicted for Cr(III) adsorption. Figs. 2 and 3 compare the predicted and experimental data for various flow rates and inlet Cr(III) concentrations, respectively. It can be observed that the model predictions compare reasonably well with the experimental

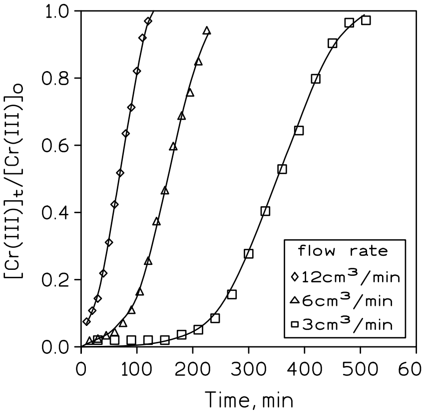

Fig. 2. Comparison of predicted (lines) and experimental (symbols) Cr(III) adsorption breakthrough curves of Amberlite 200 for different flow rates. Temperature 25°C. Inlet solution 0.1 g l^{-1} Cr(III) at pH 3.0 ± 0.05.

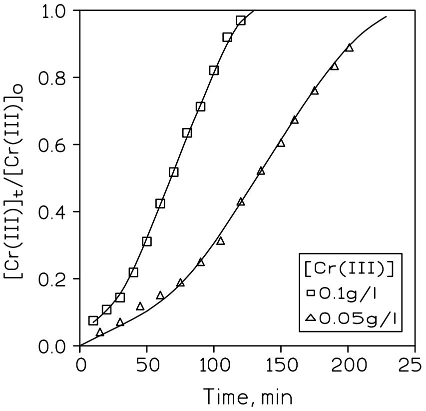

Fig. 3. Comparison of predicted (lines) and experimental (symbols) Cr(III) adsorption breakthrough curves of Amberlite 200 for different inlet metal concentrations. Flow rate 12 cm^3 min^{-1}. Temperature 25°C. Inlet solution Cr(III) at pH 3.0 ± 0.05.

data, thus, Eq. (8) can be used for convenient representation of the column ion exchange process under the present experimental conditions. A practical application of the above can be the determination of the breakthrough time, since this parameter can help to establish the optimum operating conditions of the ion exchange process. Table 6 showed the corresponding times and the breakthrough capacities, estimated from Eq. (8) under various conditions, values which closely correspond to the experimental ones. Thus, the information obtained using the model can facilitate the design and operation of the chromium (III) removal system.

3.3. Chromium elution

Regeneration and elution of chromium-loaded Amberlite 200 resin was best achieved by using NaOH solutions (Table 7). In the regeneration of Amberlite 200 resin using NaOH solution, the chromium (III) on the resin phase was replaced by exchange with Na^+ and was eluted. Fig. 4 demonstrates the percentage of chromium (III) elution as a function of the flow rate. The time to reach the complete desorption of Cr^{3+} apparently does not depend on the feed flow rate, since in both cases near 6 min are necessary to reach zero Cr^{3+} concentration in the resin, that is 17.5 or 35 BV at the flow rates of 7.5 or 15 cm^3 min^{-1}, respectively. On the other hand, regeneration at low flow rate it could be a better choice in practice than this at higher flow rate because the former avoided generating large volumes of solution.

Table 6
Comparison between experimentally and predicted values in the adsorption of Cr^{3+} by Amberlite 200 resin

Flow rate (cm^3 min^{-1})	Inlet Cr (III)[a] (g l^{-1})	Breakthrough time (min)		Breakthrough capacity (mg Crg $resin^{-1}$)	
3	0.1	210[b]	214[c]	59.9[b]	61[c]
6	0.1	64[b]	60[c]	36.4[b]	34[c]
12	0.1	2.4[b]	3[c]	2.8[b]	3.4[c]
12	0.05	21[b]	24[c]	11.7[b]	13.7[c]

[a] At pH 3.0 ± 0.05.
[b] Experimental values.
[c] Predicted values.

Table 7
Chromium (III) elution using various solutions

Solution	% Cromium elution[a]
2 M H_2SO_4	64.8
2 M HNO_3	36.5
0.1 M NaOH	10.2
0.5 M NaOH	93.1
1 M NaOH	92.0

[a] After 1 h. Resin phase: 1 g resin loaded with 3.9 mg Cr^{3+}. Aqueous solution: 20 ml. Temperature: 25°C. Stirring speed: 75 min^{-1}.

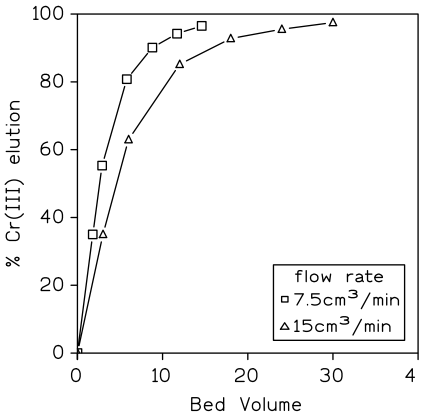

Fig. 4. The percentage of chromium (III) elution versus BV at different flow rates. Resin phase: 1 g resin loaded with 4.2 mg Cr^{3+}. Aqueous solution: 0.5 M NaOH. Temperature: 25°C.

4. Conclusions

Amberlite 200 resin had been used to remove chromium (III) from aqueous solutions. The Langmuir isotherm was found to adequately describe the equilibrium relation between the resin and liquid phases of the ion exchange process, whereas kinetics experiments showed that chromium adsorption by Amberlite 200 resin is either film-diffusion or particle-diffusion controlled at lower resin particle size, whereas at higher resin particle size the adsorption of the metal onto the resin is best represented by the shrinking core model. Under dynamic conditions, the increase in the metal concentration and the flow rate cause a decrease of the breakthrough performance. A theoretical model was adopted for representing the column performance. The model with its model parameters properly identified was observed to predict reasonably well the experimental breakthrough curves.

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