Characterization of chromium(III) removal from water using Amberlite IR120 and Amberlite IRC86

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ABSTRACT

In the present study, chromium(III) removal from aqueous solutions by a strong cationic resin (Amberlite IR120) and a weak cationic resin (Amberlite IRC86) was studied in batch experiments. In each case, the chromium exchange was examined by varying resin dosage, solution pH, contact time and initial chromium concentration. The obtained results show that the kinetics of chromium removal in the case of the two resins is rapid and follows the pseudo-second-order model. The chromium diffusion to IR120 resin can be described by either film diffusion or particles diffusion. In the case of IRC86, only film diffusion can be appropriate. At pH < 3.5, IR120 is significantly more efficient for Cr(III) removal than IRC86. The maximum exchange capacities determined by the Langmuir equation are 112 mg/g at pH 3 for IR120 and 22 mg/g at pH 4 for IRC86.

Keywords: Chromium(III); Ions exchange; Kinetic; Isotherm; Water treatment

1. Introduction

Heavy metals are common pollutants in the aquatic environment. Their major sources are metal extraction, tannery fabrication, battery manufacturing and surface finishing [1–5]. Chromium is one of these metals. In the aquatic environment, chromium can be as found in two stable oxidation states. Cr(III) is considered an essential element and Cr(VI) is recognized as toxic. The removal of Cr(III) has attracted increasing interest in view of its oxidation to harmful Cr(VI) in the presence of oxidants in soil and water [6]. Many techniques have been proposed for the removal of heavy metals from aqueous solutions such as chemical precipitation, adsorption, electrochemical treatment, reverse osmosis and membrane technologies [7–10]. Recently, the main objective of wastewater treatment is becoming the development of methods that provide the possibility of utilizing the extracted components. Ion-exchange purification is one of the attractive methods [11]. The use of synthetic resins is the method of choice in many water treatment processes for removing inorganic contaminants in wastewater [12]. With respect to traditional treatment, the pretreatment of tannery wastewater by ion exchange process for Cr(III) removal and recovery has shown a decrease in the use of chemical compounds, a reduction of sludge production and lower costs for sludge treatment and disposal [13]. Several exchange resins have been tested for Cr(III) removal such as Indion 790 [14], Lewatit S 100 [15], Amberlite IRC-5 [16],

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Amberlyst-15 [17] and Amberlite 150 [18]. From the point of view to look for other resins with faster kinetics and higher capacity, the objective of the present study is to evaluate the performance of commercial IR120 and IRC86 ion exchange resins for chromium(III) removal in aqueous solution.

2. Material and methods

2.1. Resins characterization

Amberlite IR120 is a macroporous resin with a matrix styrene-divinylbenzene copolymer. Amberlite IRC86 is a gel polyacrylic copolymer. The two resins are cationic with strong acid function in the case of IR120 and weak acid function in the case of IRC86. In the Fourier transform infrared spectroscopy (FTIR) spectrum of Amberlite IRC86, the symmetric and the asymmetric stretching bands of carboxylic acid are observed at 1,388.7 and 1,624 cm^{-1} (Fig. 1). In the case of IR120 (Fig. 1), the bands observed at 1,006.8; 1,037.6 and 1,122.5 are attributed to SO_3 symmetric stretching [19]. Thermal analysis shows that the two resins are stable at a temperature lower than 200°C. The weight loss observed in this temperature range in the case of Amberlite IR120 is due to adsorbed water characterized by the endothermic peak observed in the differential thermal analysis curve at about 100°C (Fig. 2).

2.2. Chromium sorption experiments

All chemicals reagents used in this study were of analytical grade. Firstly, the two resins were pretreated by HCl, and then washed with distilled water. The stock chromium solution was prepared by using $Cr(NO_3)_3 \cdot 9H_2O$. The pH was adjusted by adding NaOH or HCl solutions.

The chromium removal was performed in batch experiments. The effects of resins dose, contact time, chromium concentration and pH were evaluated. In all experiments, chromium analysis was performed in solutions obtained after centrifugation. The removal progress was measured by determining the concentration of Cr(III) after conversion to Cr(VI) by oxidation using H_2O_2 in an alkaline medium at elevated temperature. The formed Cr(VI) was determined using a UV-Visible Shimadzu 1650 PC spectrophotometer. The efficiency of chromium removal was calculated from the difference between the initial and the final concentrations.

3. Results and discussion

3.1. Effect of the resin dose

The percentage removal increases with increasing resins doses (Fig. 3), providing greater exchange sites. For the chromium concentration tested (50 mg/L), the maximum uptake is obtained with a dose of 1 g/L in the case of IR120 and 2.5 g/L in the case of IRC86. For a dose of 1.5 g/L, the exchange capacity of IR120 (97.6%) is about two-fold higher than that of IRC86 (52%).

3.2. Kinetic study

As shown in Fig. 4, the chromium residual concentration decreases rapidly within the first 10 min then gradually to attain equilibrium after 60 min for the two resins. At pH 3, exchange capacities at equilibrium are 24 mg/g and 7 mg/g for IR120 and IRC86 respectively. According to the various studies undertaken on chromium removal by cationic resins, it can be noted that the time evolution tendency of chromium exchange depends on the resin's nature. In the case of Indion 790, 92% of Cr(III) was extracted in 12 min [14]. However, in the case of Lewatit S 100, 150 min was necessary for maximal removal [15].

As a liquid-solid phase reaction, three possible mechanisms can be involved for Cr(III) fixation onto the resins. They include respectively: ions diffusion from the aqueous phase to the resin surface, their diffusion within the resin and their chemical reaction with the resin functional groups [20]. In the present study, kinetic modeling using the
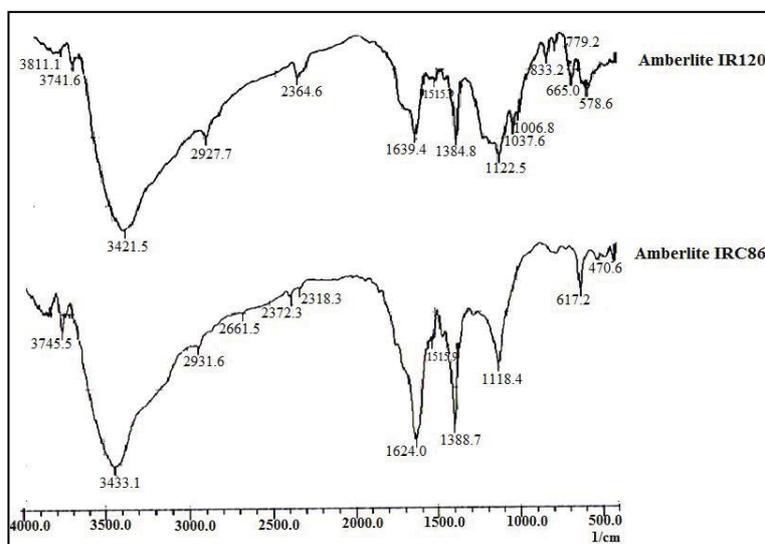

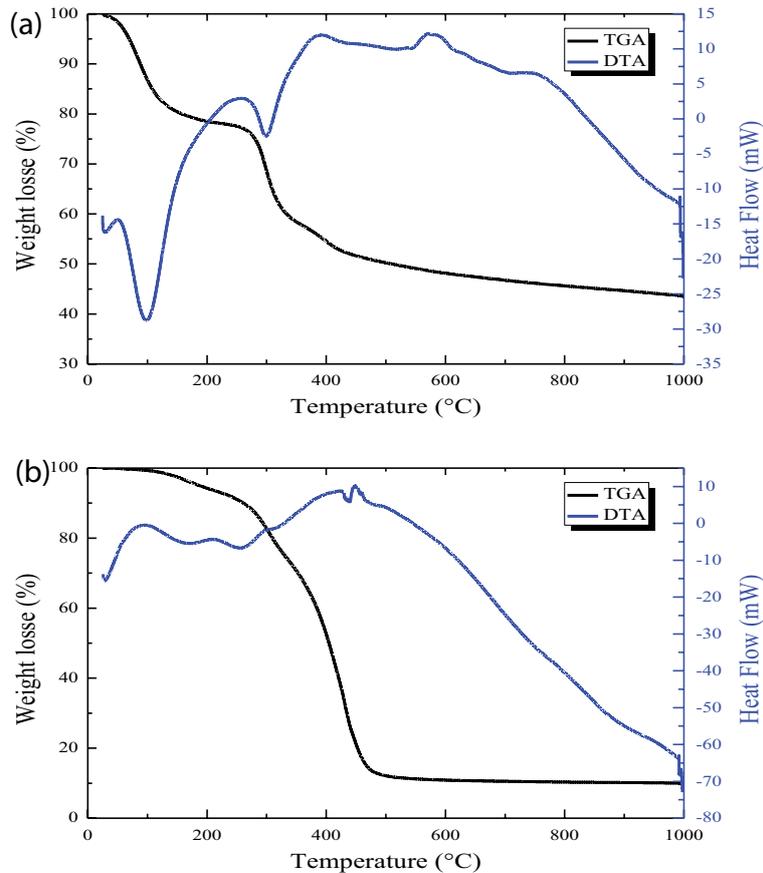Fig. 1. FTIR spectra of Amberlite IR120 and Amberlite IRC86.

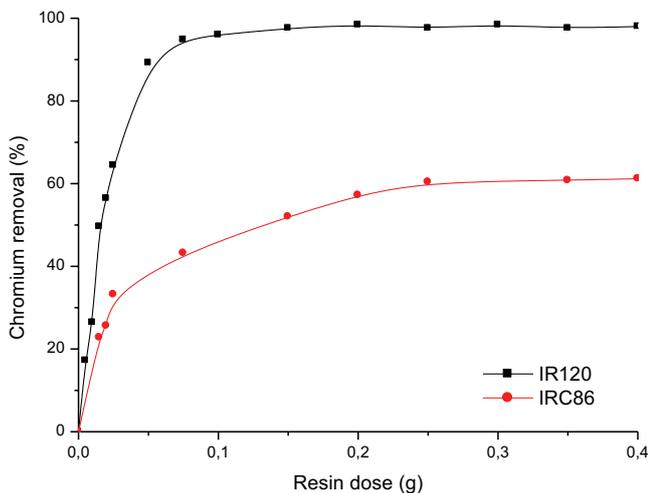Fig. 2. Thermal analysis of Amberlite IR120 (a) and Amberlite IRC86 (b).

Fig. 3. Effect of resin dosage on chromium(III) removal (C_0: 50 mg/L; t: 60 mn; pH: 3).

equations of pseudo-first-order, pseudo-second-order and diffusion is applied to the experimental data.

According to the results presented in Figs. 5 and 6, it can be noted that either the pseudo-first-order or the pseudo-do-second-order kinetics can be appropriate to describe the experimental data for both IR120 and IRC86. The calculated parameters (Table 1) show that for the first model, the chromium exchange can be characterized by approximately the same rate constants for the two resins. However, in the case of the second model, the exchange process is more rapid in the case of IRC86. In the two cases, the exchange capacity calculated at equilibrium (Q_e) is more reasonable in the case of the pseudo-second-order model. Consequently, both chromium concentration and resin quantity are responsible for the kinetics exchange. This result is not in agreement with what has been obtained for other resins; for example, the chromium kinetics exchange using IRN77 [6] and Indion 790 [14] were best described by the pseudo-first-order model.

In order to assess the nature of the diffusion process responsible for the removal of chromium by the two resins, models of intraparticle diffusion and film diffusion are used. Their linear equations are presented in Figs. 7 and 8 respectively. They reveal that the two models are appropriate to describe the chromium exchange in the case of IR120. Similar results have been observed in the case of Amberlite IRC50 (Na), where the chromium sorption kinetics has been well described by the two equations [16]. However, chromium diffusion in the case of IR86 is best modeled by the film diffusion model.

3.3. Effect of pH

Fig. 9 shows the evolution of chromium removal in the pH range 2–7. At higher pH, Cr(III) ions might precipitate.
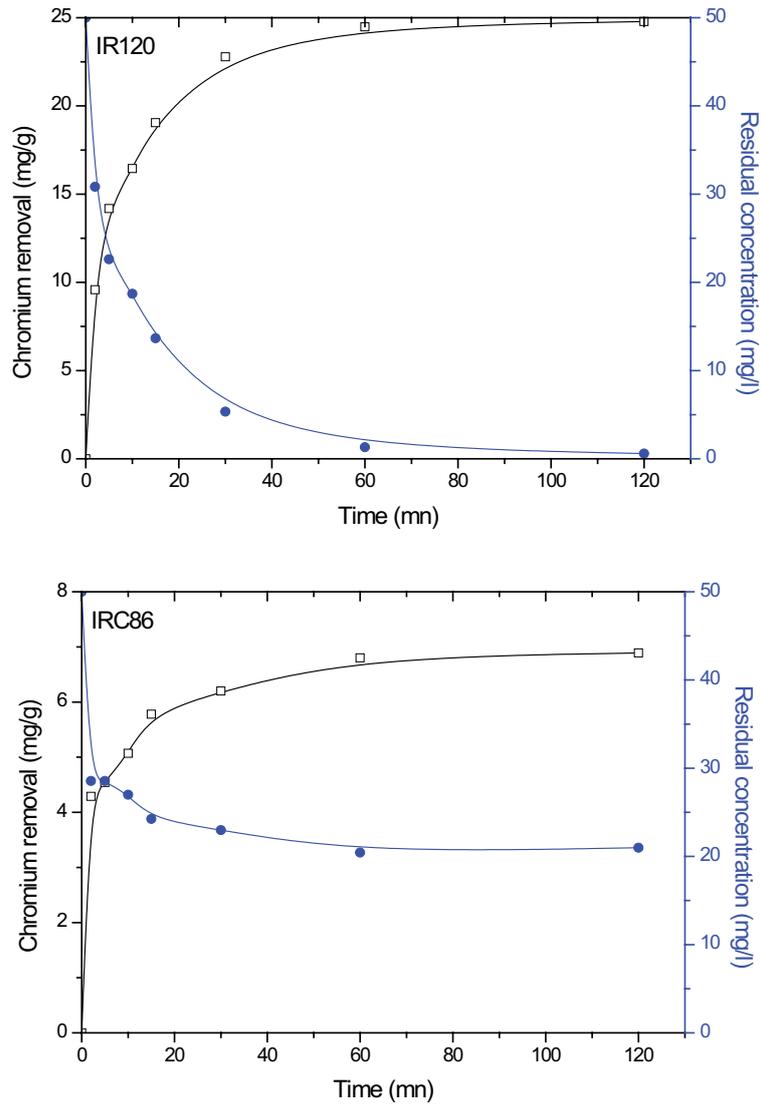
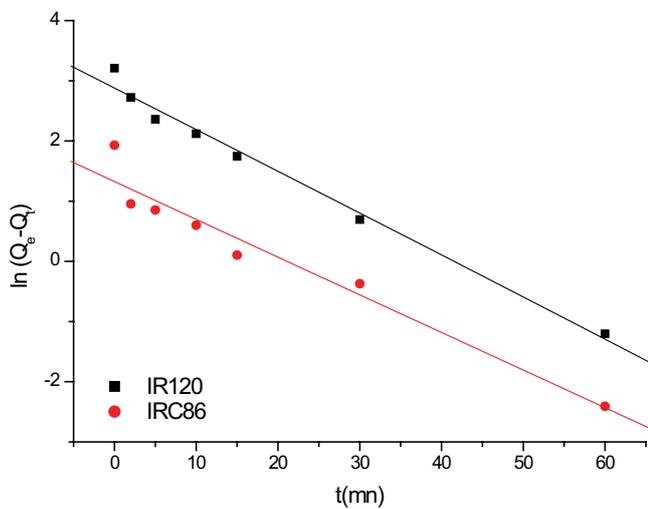Fig. 4. Effect of time on chromium(III) removal (C_0: 50 mg/L; resin dose: IR120 (2 g/L); IRC86 (5 g/L); pH: 3).
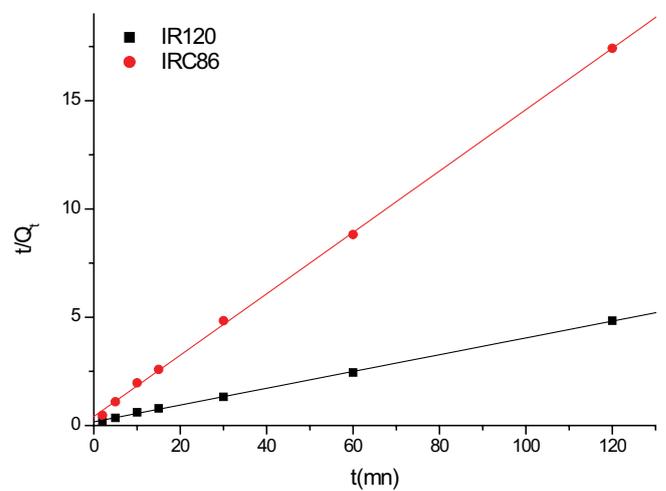

Fig. 5. Pseudo-first-order kinetics plots.

Fig. 6. Pseudo-second-order kinetics plots.

Table 1
Kinetics parameters

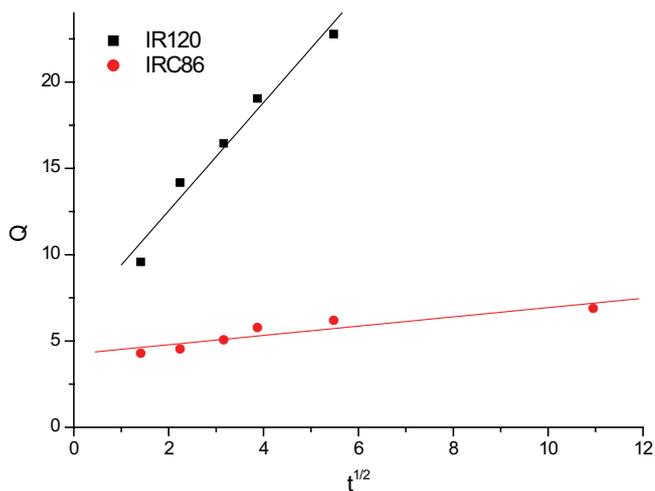| Model		IR120			IRC86		
Pseudo-first-order	R	k (min^{-1})	Q_e (mg/g)	R	k (min^{-1})	Q_e (mg/g)	
$\ln\left(Q_e - Q_t\right) = \ln Q_e - Kt$	0.994	0.0696	17.75	0.974	0.0626	3.78	
Pseudo-second-order	R	k (g mg^{-1} min^{-1})	Q_e (mg/g)	R	k (g mg^{-1} min^{-1})	Q_e (mg/g)	
$\dfrac{t}{Q_t} = \dfrac{1}{KQ_e^2} + \dfrac{1}{Q_e}t$	0.999	0.0088	25.79	0.999	0.0484	7.05	
Intraparticle diffusion	R	k (mg g^{-1} min$^{-1/2}$)		R	k (mg g^{-1} min$^{-1/2}$)		
$Q_t = K\sqrt{t} + C$	0.985	3.1381		0.920	0.2687		
Film diffusion	R	k (min^{-1})		R	k (min^{-1})		
$\ln\left(1-F\right)^2 = -Kt \left(F = \dfrac{Q_e}{Q_t}\right)$	0.994	0.0696		0.974	0.0626		

Fig. 7. Intraparticle diffusion plots.
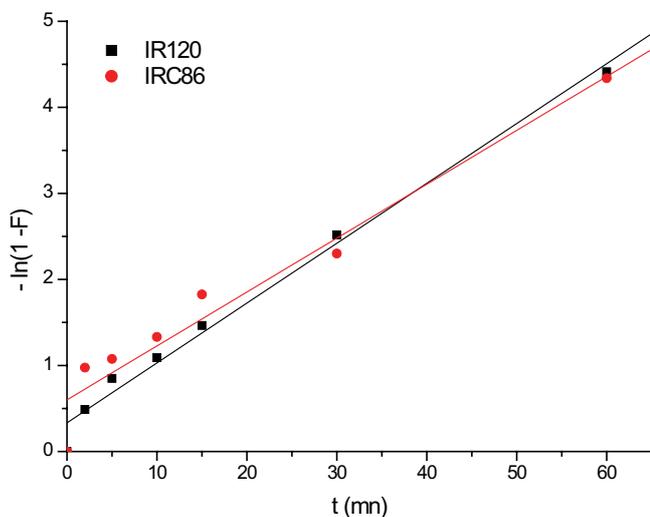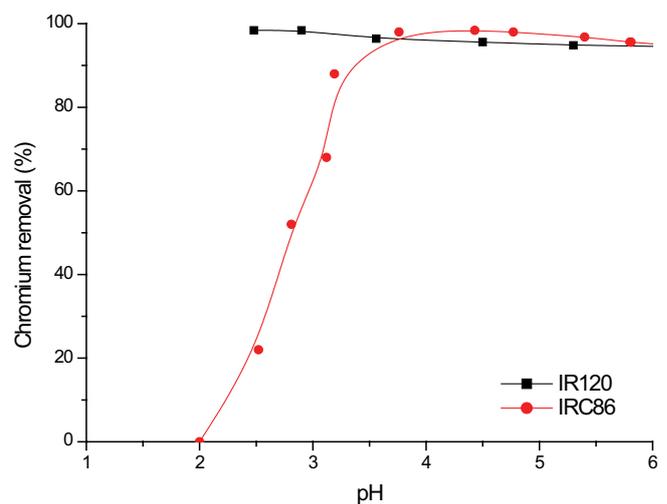

Fig. 8. Film diffusion plots ($F = Q_e/Q_t$).

Fig. 9. Effect of pH on chromium(III) removal (C_0: 50 mg/L; t: 60 mn; resin dose: IR120 (2 g/L); IRC86 (5 g/L).

The behavior of the two resins vs. chromium exchange is different in very acidic pH range (pH < 4). At greater pH, the efficiency of chromium removal by the two resins is reasonably high. In the case of IRC86, chromium removal increases to reach the maximum at pH 3.7, then decreases slightly in the pH range 4–6. This sorption trend observed at low pH is ascribed to the competitive effect between Cr(III) and hydrogen ions for the sites of the resin. In the case of IR120, significant chromium removal is observed within the pH range studied. When the pH is increased, chromium removal by IR120 decreased slightly then remained almost constant. A similar trend has been reported for extraction of Cr(III) with Indion 790, where it was found that the extraction of chromium remained almost constant (92%) within the pH range 0.5–3.5 and decreased beyond pH 3.5 [14].

The chromium exchange behavior can be attributed to its speciation in solution. The distribution diagram illustrated in Fig. 10 shows that at 2 < pH < 4, both Cr(III) and
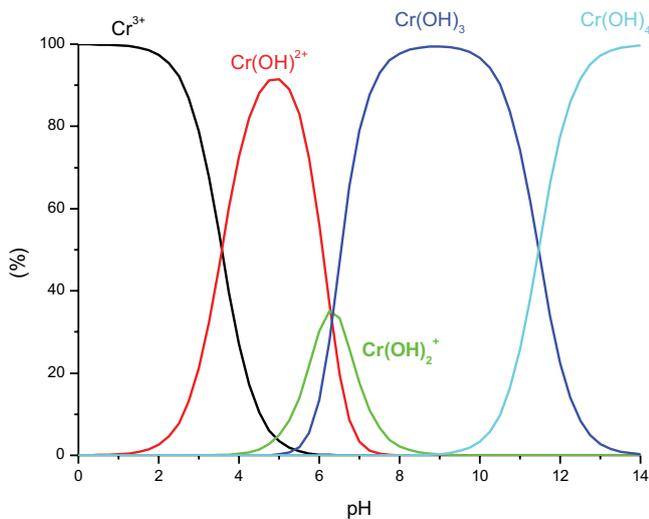
Fig. 10. Chromium speciation diagram.

Fig. 11. Experimental Isotherms of chromium(III) removal (t: 60 mn; resin dose: IR120 (1 g/L); IRC86 (5 g/L).

$Cr(OH)^{2+}$ species exist. In the pH range 4–6, the main species is $Cr(OH)^{2+}$. Consequently, in the case of IR120, the two chromium species are involved in the exchange process. However, in the case of IRC86, chromium is mainly retained as $Cr(OH)^{2+}$.

3.4. Equilibrium study

According to the results of Cr(III) removal by the two resins in the function of pH, the effect of the initial chromium concentration has been evaluated at pH: 4 for IRC86 and at pH: 3 for IR120. When the initial concentration is enhanced, a proportional increase of chromium amount exchanged per unit mass of resins is observed. The experimental isotherms are presented in Fig. 11. At the used experimental removal conditions, IR120 resin is approximately three-fold more efficient in removing chromium ions than IRC86 resin.

The experimental data are modeled using the Langmuir and the Freundlich models. The linear equations are shown in Figs. 12 and 13 and the calculated parameters are summarized in Table 2. The Langmuir equation fits well the chromium exchange by the two resins. However, the Freundlich isotherm can only describe chromium uptake by IRC86.

At the solution pH used in each case, the maximal exchange capacity is about 112 mg/g for IR120 and 23 mg/g for IRC86. These values are greater in the first case and identical in the second case to the exchange capacities obtained by other resins tested in Cr(III) removal (Table 3).

4. Conclusion

The results of the present study show that IR120 and IRC86 resins are useful in chromium(III) recovery applications. Whatever the solution pH, IR120 is significantly efficient for Cr(III) removal. However, IRC86 can be used at pH > 4. In the optimal conditions, IR120 is more efficient for Cr(III) removal than IRC86. The exchange capacities calculated by the Langmuir equation are about 112 mg/g in the case of IR120 and 23 mg/g in the case of IRC86. In the two
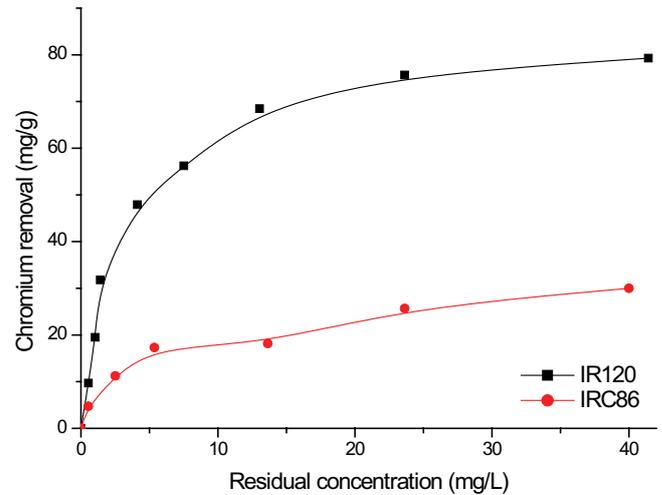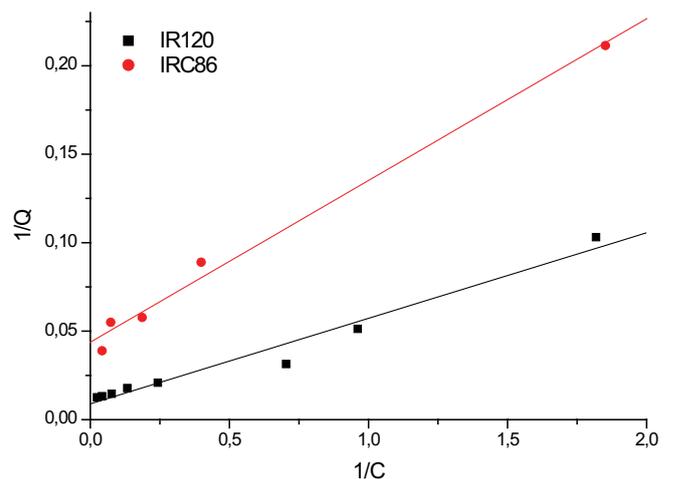

Fig. 12. Langmuir plots.
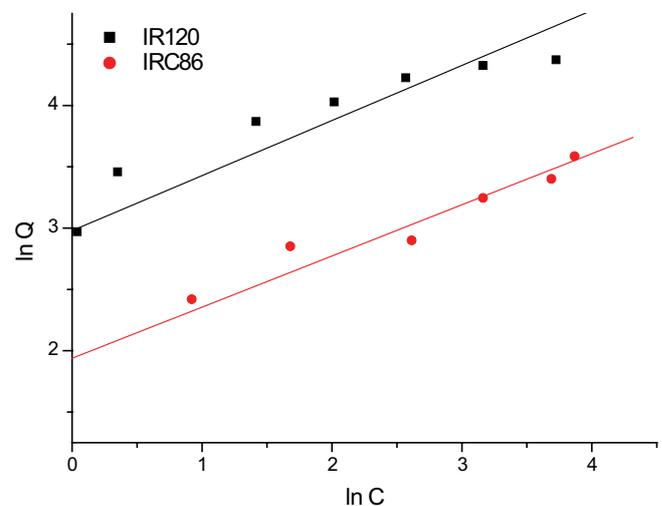
Fig. 13. Freundlich plots.

Table 2
Isotherms parameters

Resin	Model	R^2	K	n	Q_{max} (mg/g)
IR120	Langmuir	0.984	0.1845	–	112.11
	$\dfrac{1}{Q} = \dfrac{1}{Q_{max}K} \times \dfrac{1}{C_r} + \dfrac{1}{Q_{max}}$				
	Freundlich	0.937	19.6687	2.23	–
	$\ln Q = \dfrac{1}{n}\ln C_r + \ln K$				
IRC86	Langmuir	0.995	0.4790	–	22.85
	Freundlich	0.983	6.9458	2.40	–

Table 3
Exchange capacities of various resins for Cr(III)

Resin	Exchange capacity (mg/g)	Reference
Lewatit S 100	20.3	[15]
IRN77	35.4	[21]
SKN-1	46.3	[21]
Indion 790	86.9	[14]
IRC86	23	The present study
Amberlite IR120	112.1	The present study

cases, the Cr(III) removal kinetics depends on the resin dose and the chromium concentration. Chromium transfer from aqueous solution to the two resins can be well described by film diffusion model.

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