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Research Article

Cr(III) and Cr(VI) REMOVAL FROM WASTE WATER BY AMBERLITE IRN150

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ABSTRACT

The aim of this work is the use of Amberlite IRN 150 resin in the removal of Cr(III) and Cr(VI) from tanning and chrome plating waste waters respectively. Removal experiments were carried out in batch. Kenitics and equilibrium studies were undertaken using various models. The obtained results show that the increase in pH implies an increase of Cr(III) removal in tanning water and a decrease of Cr(VI) removal in chrome plating water. In the two cases, the exchange kinetics is well described by the second order model. The removal of the two ions by IRN150 is not limited by intraparticular diffusion. The Freundlich isotherm is more suitable for describing Cr(III) removal in tanning water. However, in chrome plating water, Cr(VI) removal is better described by the Langmuir isotherm.

Keywords: Cr(III); Cr(VI); Amberlite IRN150; Tanning; Chrome plating; Water treatement.

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1. INTRODUCTION

Chromium is found in all compartments of the environment. It can be found in water, air, soil and also in living organisms [1]. Rock alteration and erosion as well as precipitation are the major natural source of chromium release and its transport to surface and groundwater [2]. Generally, quantities of chromium introduced into the aquatic environment are mainly related

to industrial emissions [3]. The main chromium species in water are Cr(VI) and Cr(III). Cr(VI) is highly soluble in water. However, Cr(III) formes stable salts and hydroxides. Chromium is used in a large number of industrial applications such as metallurgy, electroplating, paints, pigments production and wood preservation [4]. The hard or decorative electrolytic chrome plating industry is the main process using Cr(VI). In this technique, a thin layer of chromium is created onto metallic surfaces. The process is based on the reduction of hexavalent chromium to metallic form by cathodic reduction [5, 6]. In Algeria, about seven companies of chrome plating industry exist. The main industy using trivalent chromium is tanning which is based on the tendency of Cr(III) to form stable complexes with proteins. This industry is considered to be particulary polluting [6, 7]. Fifteen tanneries exist in Algeria. The objective of the present study is the removal of Cr(III) from tanning water and Cr(VI) from chrome plating water by Amberlite IRN150.

2. MATERIALS AND METHODES

The exchange resin used in the present study “Amberlite IRN150” (PROLABO) has acid and basic functions. Waste waters used for Cr(III) and Cr(VI) removal are sampled respectively from EL-HADDADA tannery located in Jijel city and from SOMATEL chrome plating company specialized in the manufacture of construction machinery and machine tools and located in Constantine city (Fig. 1). The industrial process used in each case is illustrated in Fig. 2 and Fig.3 respectively. The sampled waters are characterized by high acidity and important mineralization (Table 1).

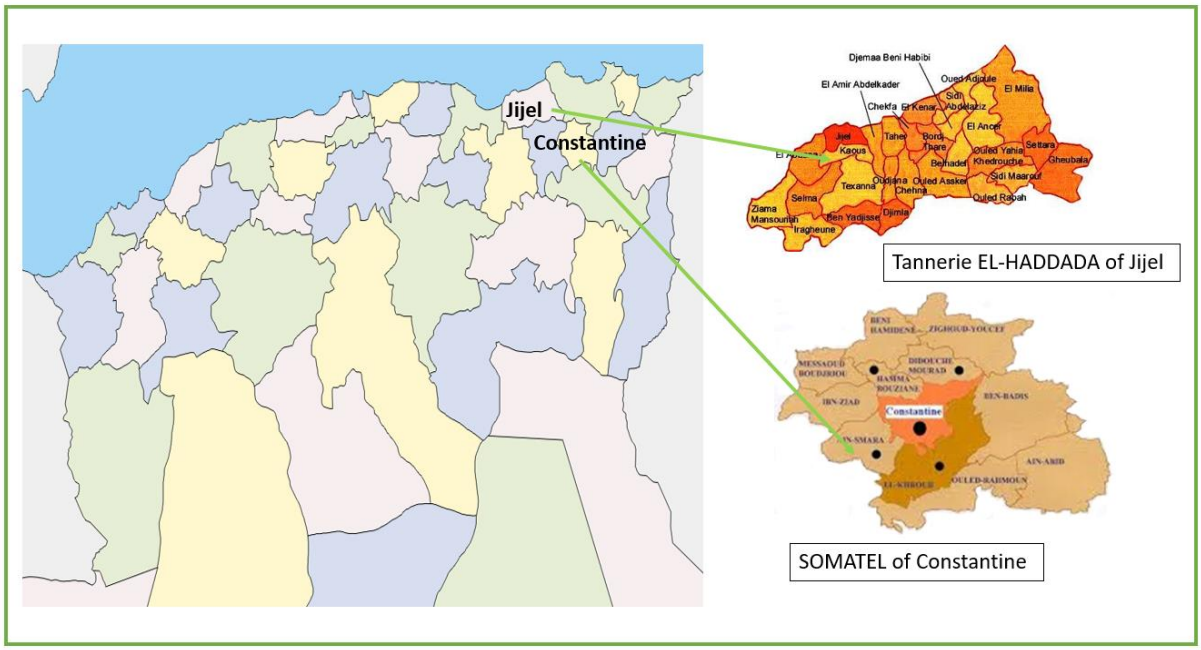

Fig.1. Location of EL-HADDADA tannery and SOMATEL chrome plating company

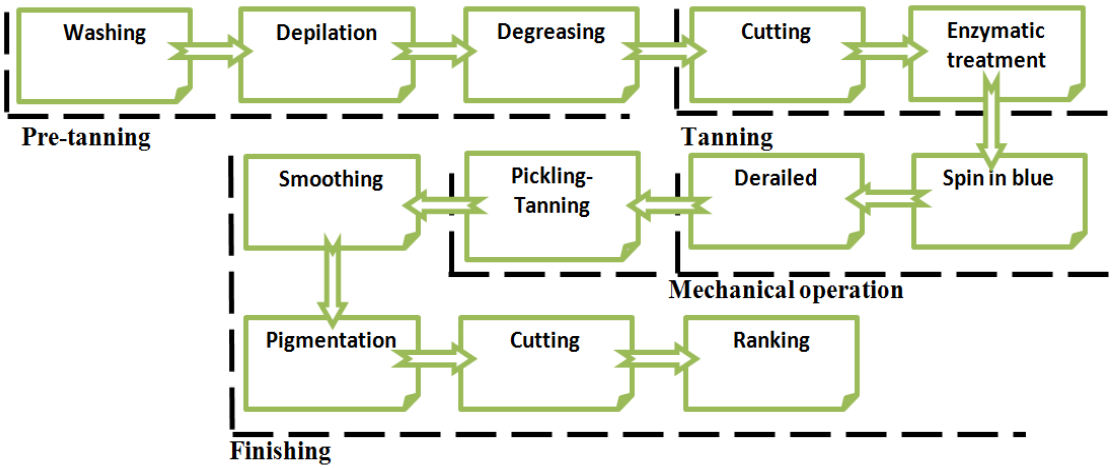

Fig.2. Diagram of El-Haddada tanning process

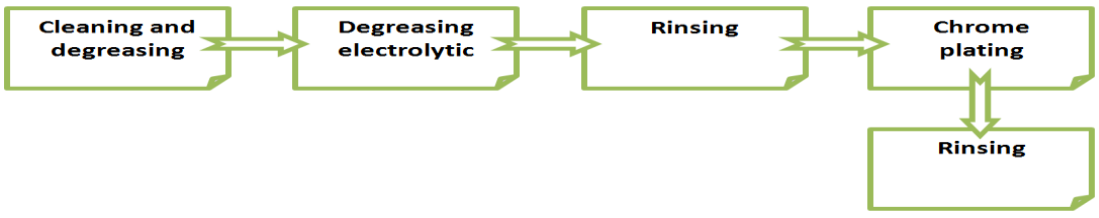

Fig.3. Diagram of SOMATEL chrome plating process

Table 1: Wastewater analysis

parametre	Tannery water	Chrome plating water
pH	4.03	2.10
C.E ($ms.cm^{-1}$)	59.90	19.68
Cl^- ($mg.L^{-1}$)	13.85	390.50
SO_4^{2-} ($mg.L^{-1}$)	16.64	12.97
Fe^{3+} ($mg.L^{-1}$)	64.10	-
Al^{3+} ($mg.L^{-1}$)	355.38	-
Cr(VI) ($g.L^{-1}$)	-	**5.86**
Cr(III) ($g.L^{-1}$)	**4.17**	-

The removal experiments were carried out in batch. The effects of pH and contact time were evaluated using the waste water diluted 100 times. To evaluate the effect of the chromium initial concentration, various dilutions were used. In all the experiments, a resin dose was mixed with the diluted waste water at room temperature. The pH was adjusted by adding NaOH or HCl solution (1 $mol.L^{-1}$). The formed suspensions were magnetically stirred for one hour. After centrifugation, residuel concentrations of the chromium species were measured in the recovered solution by UV-visible spectrophotometer (Shimadzu 1650PC).

3. RESULTS AND DISCUSSION

3.1 Effect of pH

As shown in Figure 4, the pH increase implies the enhancement of Cr(III) removal from tanning water. This behavior is identical to that recorded in several studies of Cr(III) removal by cation exchange resins [8-10]. However, the Cr(VI) removal in chrome plating water decreases significantly from pH: 5 and no removal is observed at pH greater than 7. In the case of several anion exchange resins, it was also shown that the maximum Cr(VI) exchange is obtained in the pH range ($1 \leq pH \leq 5$) and that the removal decreases strongly with the increase in pH [11].

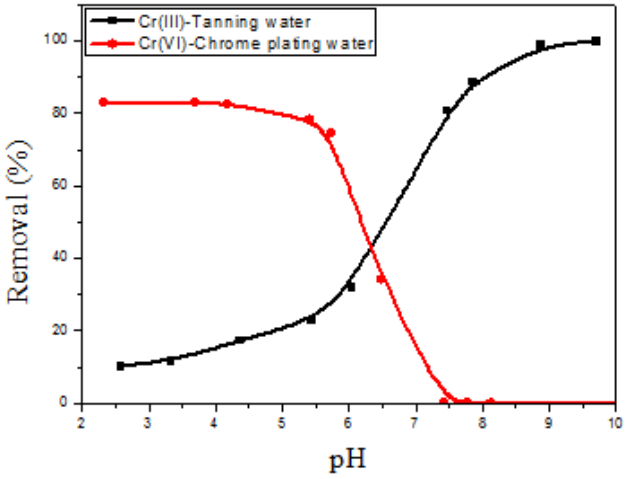

Fig.4. Effect of pH Cr(III) and Cr(VI) removal by IRN150 (resin dose: 1 $g.L^{-1}$, t: 60 min)

3.2 Effect of contact time

The evolution of the two chromium species removal as a function of time is characterized by two steps (Fig. 5). The first quick step does not exceed 20 minutes in the case of tanning water and 30 minutes in the case of chrome plating water. Cr(III) removal seems to be more rapid.

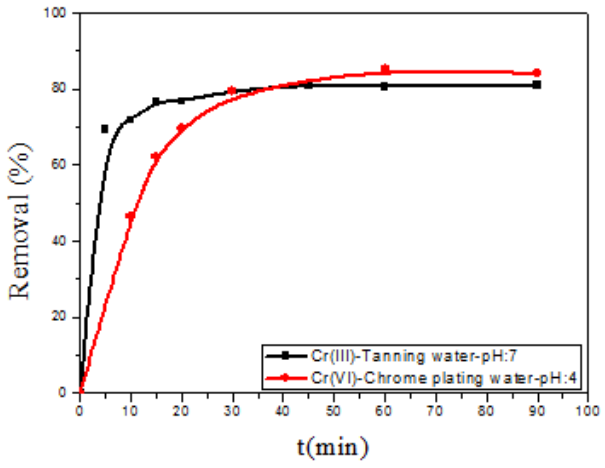

Fig.5. Effect of time on Cr(III) and Cr(VI) removal by IRN150 (resin dose: 1 $g.L^{-1}$)

In order to model the exchange kinetics of the two ions, the first and the second order models are used. In the first model, the kinetics is expressed by the following equation:

$$\frac{dQ_t}{dt} = k_1\,(Q_e - Q_t) \quad \text{.....(1)}$$

The integration of this equation gives the linear equation:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1\, t \quad \text{.....(2)}$$

According to the second model, the kinetics is expressed by the following equation:

$$\frac{dQ_t}{dt} = k_2\,(Q_e - Q_t)^2 \quad \text{.....(3)}$$

The integration of this equation gives the linear equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad \text{.....(4)}$$

Q_e and Q_t adsorption capacities of IRN 150 at equilibrium and time t.

k_1: the first order rate constant (min^{-1}).

k_2: the second order rate constant ($mg.g^{-1}.min^{-1}$).

The obtained results are represented in Figures 6 and 7 and the calculated parameters are presented in Table 1. The near perfect linearity between t/Q_t and t indicates that the second order model is more suitable for describing Cr(III) and Cr(VI) removal.

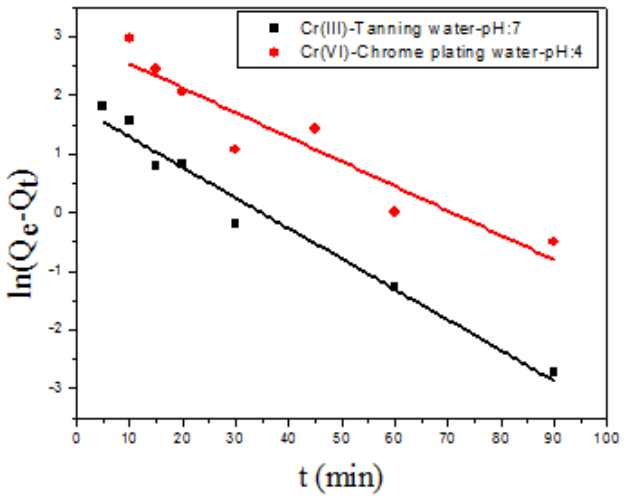

Fig.6. First order kinetics of Cr(III) and Cr(VI) removal by IRN150

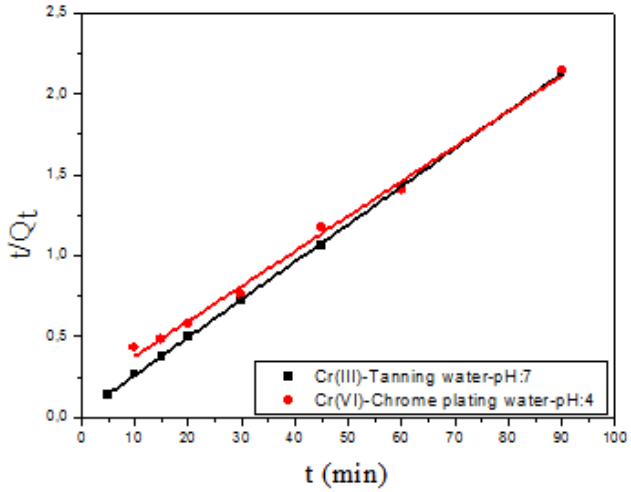

Fig.7. Second order kinetics of Cr(III) and Cr(VI) removal by IRN150

Table 2. Kinetic parameters of Cr(III) and Cr(VI) removal by IRN150

Ion	First order model	Second order model
Cr(III)	R^2= 0.968 k_1= 0.0015 (min^{-1}) Q_e= 19.23 ($mg.g^{-1}$)	R^2= 0.999 k_2= 0.0214 ($mg.g^{-1}.min^{-1}$) Q_e = 42.83 ($mg.g^{-1}$)
Cr(VI)	R^2= 0.874 k_1= 0.0006 (min^{-1}) Q_e= 23.90 ($mg.g^{-1}$)	R^2= 0.994 k_2=0.0029 ($mg.g^{-1}.min^{-1}$) Q_e = 46.17 ($mg.g^{-1}$)

In addition to the previous models, the experimental kinetic data are also analyzed using diffusion models. The equation of intraparticle diffusion model is:

$$Q_t = k_{id}\, t^{1/2} + C \quad \text{.....(5)}$$

k_{id}: the intra-particle diffusion rate constant and C: Constant.

In the case of the two ions, the representation of the experimental data using the intraparticular diffusion equation, shows that this model is not involved in the removal process.

Two external diffusion models with the following equations are also applied:

$$-\ln(1-F) = k\, t \quad \text{.....(6)}$$

$$-\ln(1-F^2) = k\, t \quad \text{.....(7)}$$

F: the ratio of the adsorbed quantity to the quantity adsorbed at equilibrium ($F=(q_t/q_e)$) and k: diffusion constant.

According to the obtained results (Figs. 8, 9), only the kinetics of Cr(VI) removal can be described by the external diffusion models.

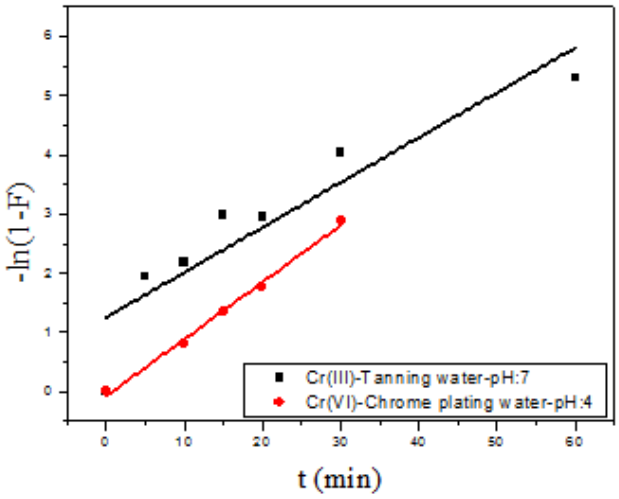

Fig.8. Film diffusion kinetics of Cr(III) and Cr(VI) removal by IRN150

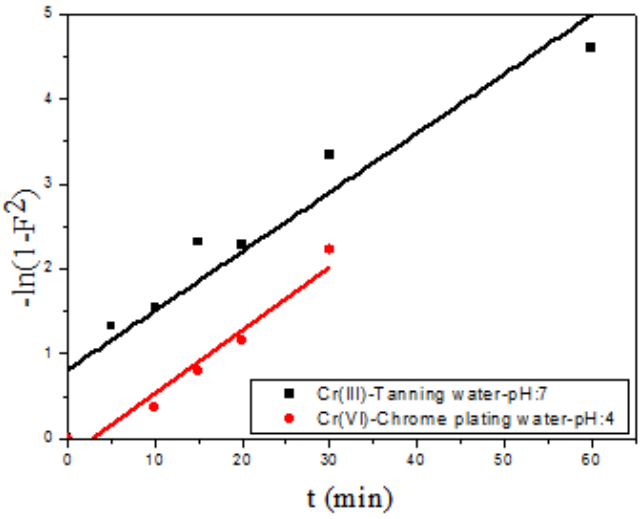

Fig.9. Interparticles diffusion kinetics of Cr(III) and Cr(VI) removal by IRN150

Table 3. Diffusion parameters of Cr (III) and Cr (VI) removal by IRN150 resin

Ion	Intraparticular Diffusion	Film Diffusion	Interparticles Diffusion
Cr(III)	R^2= 0.620	R^2= 0.814	R^2= 0.886
	k_{id}= 10.90 (mg.g^{-1}.min$^{-1/2}$)	k= 0.0760 (min^{-1})	k= 0.0697 (min^{-1})
Cr(VI)	R^2= 0.990	R^2= 0.992	R^2= 0.935
	k_{id}=14.95 (mg.g^{-1}.min$^{-1/2}$)	k= 0.0963 (min^{-1})	k= 0.0747 (min^{-1})

3.3. Effect of initial concentration

The increase of Cr(III) concentration in tanning water at pH 7 implies a large increase in the removed amount. This can be also due to Cr(III) precipitation. A saturation is observed in the case of Cr(VI) removal (Fig. 10).

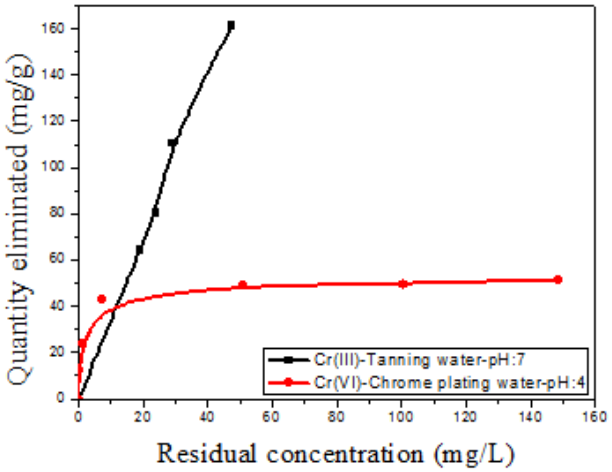

Fig.10. Isotherms of Cr(III) and Cr(VI) removal by IRN150 (resin dose: 1 g.L^{-1}, t: 60 min)

The Langmuir and the Freundlich equations are used to model the experimental data. The Langmuir isotherm assumes that all the surface sites are identical with no interaction between the adsorbed molecules which are organized in monolayer. However, according to Freundlich, the adsorption sites are not identical. According to the first model, the adsorbed quantity is related to the maximum adsorption capacity (Q_m) and the concentration of the equilibrium solute (C_{eq}) by the equation:

$$\frac{Q}{Q_m} = \frac{K_L C_{eq}}{1 + K_L C_{eq}} \quad \text{.....(8)}$$

The linear equation is:

$$\frac{C_{eq}}{Q} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_{eq} \quad \text{.....(9)}$$

The Freundlich equation is written as:

$$Q = K_F \, C_{eq}^{1/n} \quad \text{.....(10)}$$

The linearization of the Freundlich relation leads to the equation:

$$\ln Q = \ln K_F + \frac{1}{n} \ln C_{eq} \quad \text{.....(11)}$$

K_F and n: Freundlich parameters, characteristics of the solution and of the adsorbent.

The obtained results (Fig. 11, 12) show that in the case of Cr(III), the experimental isotherm can be described only by the Freundlich equation, confirming the possible Cr(III) precipitation. In the case of Cr(VI) removal, the Langmuir equation is more suitable. This result is in agreement with what has been obtained in a study of Cr(VI) removal in industrial water by Ambersep 900 and Ambersep 132 resins [12].

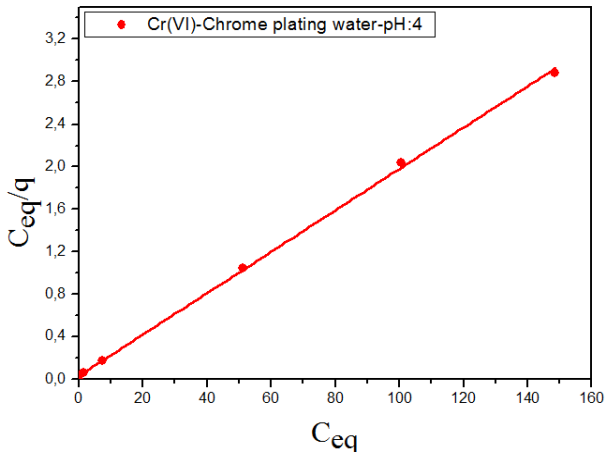

Fig.11. Langmuir isotherm of Cr(VI) removal by IRN150

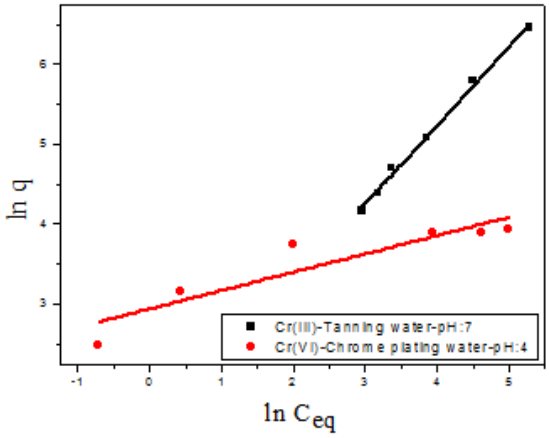

Fig.12. Freundlich isotherm of Cr(III) and Cr(VI) removal by IRN150

Table 4. Isotherms parameters of Cr(III) and Cr(VI) removal by IRN150

Ion	Langmuir model	Freundlich model
Cr(III)	-	R^2= 0.994 K_F= 3.67 (mg.g^{-1}) n= 0.98
Cr(VI)	R^2= 0.999 K_L= 0.63 (L.mg^{-1}) Q_m= 51.36 (mg.g^{-1})	R^2= 0.812 K_F=18.85 (mg.g^{-1}) n= 0.98

4. CONCLUSION

According to the results of the present study, it can be concluded that the resin Amberlite IRN 150 can be used at pH ≥ 7 for Cr(III) removal in tanning water and at pH<5 for Cr(VI) removal in chrome plating water. IRN 150 is more efficient for Cr(III) removal in tanning waters than for Cr(VI) removal in chrome plating water where the effect of the presence of competitive ions is more important. In both cases, the removal kinetics is better described by the second order model. The experimental isotherm of Cr(III) removal from tanning water follows the Freundlich model. However, the Langmuir equation is more suitable for the removal of Cr(VI) in chrome plating water.

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