

SELECTIVE LIQUID-SOLID EXTRACTION OF Cr (III) FROM Cr (III) AND Fe (III) MIXTURE BY CHELEX 100 RESIN

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Abstract: This work focuses on the liquid-solid extraction of the mixture chromium (III) and iron (III) by the resin Chelex 100. The influence of operating parameters as equilibrium time (2 to 45 min), the initial pH of aqueous solution (1.06 to 3.97), effect of initial chromium (III) and iron (III) concentrations (100 to 500 ppm), effect of temperature (295 to 328 K) and the effect of ionic strength (NaCl, KNO₃) was studied. The extraction yields of and the capacities of sorption of Cr (III) and Fe (III) by the resin Chelex 100 were determined at 64.94 and 87.30 % equivalent to 11.6 and 10.94 mg·g⁻¹ respectively. The equilibrium time was 45 and 5 min for initial concentrations of the mixture of Cr (III) and Fe (III) 500 mg·L⁻¹ respectively. The kinetic model of the pseudo second order describes the sorption process for the two metals. The separation of two metals is maximal at 100 mg·L⁻¹ and in the presence of KNO₃ 0.1 M. The thermodynamic study showed that the extraction process is exothermic (-29223 and -20735.1 kJ·mol⁻¹ for Cr (III) and Fe (III) respectively) and the negative ΔG values show that, the sorption of metals occurs spontaneously in 295 - 328 K, while it is not appropriate in case of Fe (III) as indicated by the positive sign of ΔG (96 kJ·mol⁻¹) at 309 K. The percentage of desorption is estimated to 57.6 % for both metals by the solution of HNO₃ 1 M. The experimental results obtained showed the validity of the liquid-solid extraction to be used for selective extraction and concentration of Cr (III) from the Cr (III) and Fe (III) mixture solutions.

Keywords: *Chelex 100, diffusion models, kinetic models, liquid-solid extraction, thermodynamic parameters*

INTRODUCTION

Urbanization, industrial development, and heavy traffic lead to contamination of waters with heavy metals [1]. The extensive use of chromium in leather tanning, metallurgy, electroplating and other industries has resulted in the release of aqueous chromium to the subsurface at numerous sites. The most common oxidation states for chromium are +3 and +6. Chromium (III) cannot be absorbed, and can form complex with protein in the external layer of skin and accumulate in the lung causing lung cancer. Thus, scholars pay more and more attention to removal and recovery of chromium (III) because of the growing importance to environmental protection problems [2]. About Fe (III), great interest is still focused on the development of drugs for treatment of iron-overload based diseases, due to poor pharmacological properties of commercially available therapeutics. To control iron homeostasis a long-term administration of iron chelating agents at high doses is required, and this leads to a poor or non-compliance [3].

Solvent extraction [4], membrane separation [5], adsorption [6], bioremediation [7], ion exchange [8], etc. are the common techniques for removal and recovery of chromium from industrial waste streams.

Chelex 100 is a chelating ion-exchange resin having functional iminodiacetic acid groups in a styrene-divinylbenzene matrix [9]. It has a high selectivity for transition metals such as Co, Ni, Cu and Zn [10].

In this paper, was studied the optimization of Cr (III) extraction from Cr (III) and Fe (III) mixture by Chelex 100 resin. Various parameters have been studied as contact time, the initial concentration of mixture Cr (III) and Fe (III), initial pH and ion strength effect, to assess at the performance of Chelex 100 resin.

MATERIALS AND METHODS

Reagents

Chelex 100 was used as supplied by Bio-Rad. The gel-type macroporous resin was half in sodium form (47 % Na and 53 % H). The size of resin particles was 0.3 to 1.0 mm with capacity $0.4 \text{ mmol} \cdot \text{mL}^{-1}$ and the pH range 0 - 14.

A stock solution of $1 \text{ g} \cdot \text{L}^{-1}$ Cr (III) and Fe (III) ions were prepared by diluting an appropriate amount of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in $0.5 \text{ mol} \cdot \text{L}^{-1}$ HCl solutions (Merck Standard Solution). Other solutions of Cr (III) and Fe (III) ions were prepared from the stock solutions by appropriate dilution. All other chemicals used for experiments were of analytical reagent grade. Distilled water was used in all experiments.

Optimization of extraction parameters

In a 25 mL Erlenmeyer, 10.0 mL of the mixture of Cr (III) and Fe (III) solution at initial concentrations of $500 \text{ mg} \cdot \text{L}^{-1}$, were added at 0.2 g of Chelex 100: $T = 20 \pm 1 \text{ }^\circ\text{C}$, $\text{pH} = 2.67$, and the agitation speed of 500 rounds per minute (rpm) for a time ranging from 2 to 45 min. The residual Cr (III) and Fe (III) concentrations in the aqueous solution after treatment were measured by Atomic Absorption Spectroscopy (AAS) - Perkin Elmer (PinAAcle 900 H), of Tlemcen University.

The percent extraction [%] was determined as follows:

$$Yield (\%) = \frac{C_0 - C}{C_0} \cdot 100 \quad (1)$$

The extraction amount was calculated as follows [11]:

$$q_t = \frac{V (C_0 - C) M}{W} \quad (2)$$

q_t is the extraction amount [$\text{mg} \cdot \text{g}^{-1}$], W the weight of the Chelex 100 [g], M molar mass [$\text{g} \cdot \text{mol}^{-1}$], V the volume of solution [L], and C_0 , C are the concentrations [$\text{mol} \cdot \text{L}^{-1}$] of Cr (III) and Fe (III) ions before and after extraction, respectively.

The effect of initial pH on the equilibrium uptake of Cr (III) extraction from Cr (III) and Fe (III) mixture by the Chelex 100 was investigated between pH 1.06 - 3.97. The experiments were performed by adding a known weight of resin (0.2 g) in five flasks containing each 10 mL of the mixture of Cr (III) and Fe (III) solution. Dilute HNO_3 was used to adjust the pH of the mixture solutions using a pH-meter (model WTW, pH 3310 SET 2, Germany). The flasks were shaken at 500 rpm at 20 ± 1 °C for 45 min.

Kinetic experiments were carried out by stirring of 10 mL of the mixture of Cr (III) and Fe (III) solutions from 100 to $500 \text{ mg} \cdot \text{L}^{-1}$ added at 0.2 g of Chelex 100 in a flask for $T = 20 \pm 1$ °C, pH = 2.67 and agitation speed of 500 rpm for 45 min.

Temperature effect was studied on 10 mL of the mixture solution at $500 \text{ mg} \cdot \text{L}^{-1}$ in the range temperature 295 - 328 K.

Ionic strength effect on the Cr (III) extraction from Cr (III) and Fe (III) mixture by the Chelex 100 (0.2 g) was investigated by adding a known weight of different solids (NaCl , KNO_3) to 10 mL of $500 \text{ mg} \cdot \text{L}^{-1}$ solution at 20 ± 1 °C, pH = 2.67 and agitation speed of 500 rpm for 45 min.

Extraction kinetic models

The extraction kinetic behavior of Cr (III) and Fe (III) was analyzed with the pseudo first and the pseudo second models [12, 13].

The linear equation of pseudo first model was:

$$\ln(q_s - q_t) = \ln q_s - k_f t \quad (3)$$

q_t [$\text{mg} \cdot \text{g}^{-1}$] is the extraction capacity at the time of t ; k_f is the rate constant of the first order extraction [min^{-1}].

The linear equation of pseudo-second model was:

$$t/q_t = 1/k_s q_s^2 + t/q_s \quad (4)$$

k_s is the rate constant of the second order extraction [$\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$].

Elution study

Systematic studies have been made on the elution behavior of Cr (III) and Fe (III) with distilled water and various acids (HCl , HNO_3) of different concentrations (0.5 – 2 M). Stripped metal ions were collected and analyzed by AAS.

RESULTS AND DISCUSSION

Effect of contact time

The kinetic of extraction that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define the efficiency of sorption. Aqueous feed solutions containing $500 \text{ mg}\cdot\text{L}^{-1}$ Cr (III) and Fe (III) were contacted with 0.2 g of Chelex 100 for various time intervals and the results are depicted in Figure 1.

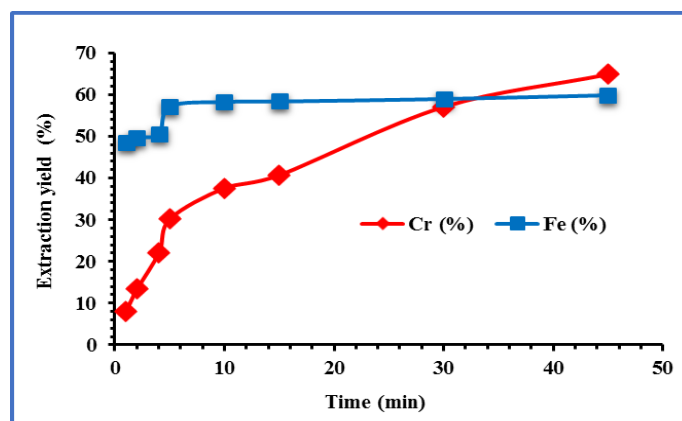


Figure 1. Effect of contact time on the ion exchange of Cr (III) and Fe (III) using Chelex 100: $[\text{Cr (III)}] = [\text{Fe (III)}] = 500 \text{ mg}\cdot\text{L}^{-1}$, $T = 20 \pm 1 \text{ }^{\circ}\text{C}$, agitation speed = 500 rpm and initial pH = 2.67

The amount of Cr (III) and Fe (III) adsorbed onto Chelex 100 increased with increase in contact time, the maximum percents of Cr (III) and Fe (III) extraction were 64.94 % and 59.9 % obtained after 45 and 5 min for initial concentrations of the mixture of Cr (III) and Fe (III) $500 \text{ mg}\cdot\text{L}^{-1}$, respectively. This is apparent from the fact that the Chelex 100 has a large number of vacant surface sites available for adsorption during the stage of extraction of the mixture. This result was similar to the result obtained in extraction of the mixture of Hg (II) and Cd (II) by the resin Chelex 100 [14].

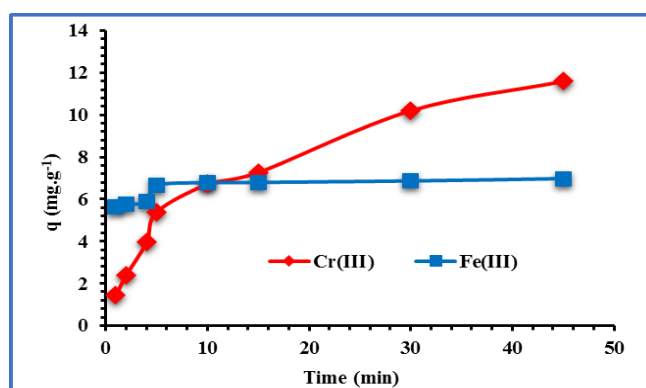


Figure 2. Effect of extraction capacity on the ion exchange of Cr (III) and Fe (III) using Chelex 100: $[\text{Cr (III)}] = [\text{Fe (III)}] = 500 \text{ mg}\cdot\text{L}^{-1}$, $T = 20 \pm 1 \text{ }^{\circ}\text{C}$, agitation speed = 500 rpm and initial pH = 2.67

The extraction capacity by the Chelex 100 resin of Cr (III) is bigger compared to Fe (III). Both metals reach the maximum of extraction to 45 min. The capacities of sorption of Cr (III) and Fe (III) by the resin Chelex 100 are 11.60 and 6.95 $\text{mg}\cdot\text{g}^{-1}$ respectively.

Kinetics of extraction

In this study, batch extraction kinetics of Cr (III) and Fe (III) ions at $500 \text{ mg}\cdot\text{L}^{-1}$ initial concentration, with the chelating resin Chelex 100 has been studied. The different values of constants from the slopes and intercepts of linear plots of equation (3) (shown in Figure 3), equation (4) (shown in Figure 4), were summarized in Table 1.

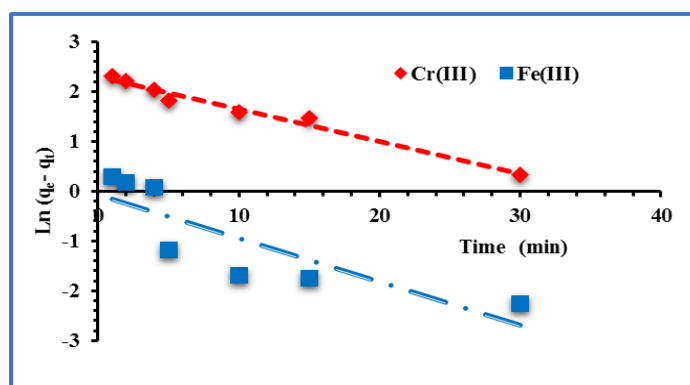


Figure 3. Lagergren plots for the extraction of Cr (III) and Fe (III) onto Chelex100: amount of resin = 0.2 g, volume of ion exchange medium = 10 mL, $T = 20 \pm 1$ °C, agitation speed = 500 rpm, initial pH = 2.67 and initial concentration of Cr (III) and Fe (III) = $500 \text{ mg}\cdot\text{L}^{-1}$

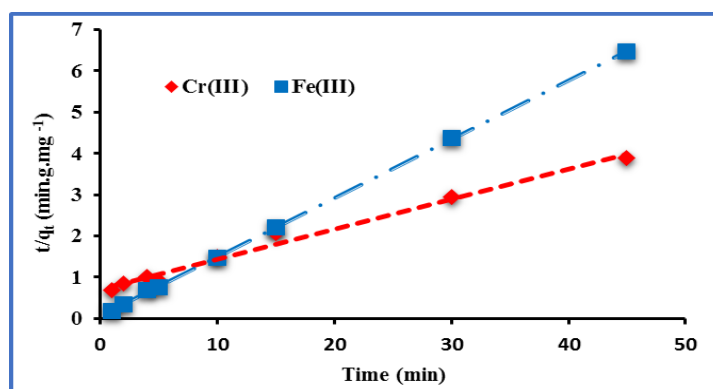


Figure 4. Pseudo second order kinetic model for the Cr (III) & Fe (III) extraction onto Chelex 100: amount of resin = 0.2 g, volume of ion exchange medium = 10 mL, $T = 20 \pm 1$ °C, agitation speed = 500 rpm, initial pH = 2.67 and initial concentration of Cr (III) and Fe (III) = $500 \text{ mg}\cdot\text{L}^{-1}$

Table 1. Kinetic parameters for extraction of Cr (III) & Fe (III) by Chelex 100

Models	Parameters	[Cr (III)] = 500 mg·L ⁻¹	[Fe (III)] = 500 mg·L ⁻¹
<i>Pseudo first order</i>	k_f [min ⁻¹]	0.065	0.087
	q_e^* [mg·g ⁻¹]	10.02	0.938
	q_e^{**} [mg·g ⁻¹]	11.60	6.954
	R^2	0.979	0.714
<i>Pseudo second order</i>	$k_s \cdot 10^3$ [g·mg ⁻¹ ·min ⁻¹]	7.302	325.2
	q_e^* [mg·g ⁻¹]	13.89	7.042
	q_e^{**} [mg·g ⁻¹]	11.60	6.954
	R^2	0.987	0.999

*calculated, **experiment

As shown in Table 1, the obtained coefficients values of the pseudo second order model (> 0.985) were better than those of the first order model (< 0.980) for the extraction of Cr (III) and Fe (III) at the considered concentrations, suggesting that the pseudo second order model was more suitable to describe the extraction kinetics of Chelex 100. This suggests that the rate limiting step may be a chemical process involving valence forces through sharing or exchange of electrons [15].

The rate law governing the extraction of Cr (III) and Fe (III) by Chelex 100 had been determined by using various experimental conditions. Three possible extraction mechanism had been evaluated if the extraction of Cr (III) and Fe (III) into the resin must be considered as a liquid-solid phase reaction which includes diffusion of Cr (III) and Fe (III) 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 were [16]:

(i) Film diffusion controlled process, the rate equation is: $-\ln(1 - F) = kt$ (5)

(ii) Particle diffusion controlled process, with the equation as: $-\ln(1 - F^2) = kt$ (6)

(iii) Moving boundary process: $3 - 3(1 - F)^{\frac{2}{3}} - 2F = kt$ (7)

Table 2. The regression coefficients and rate constants for the tested extraction mechanisms of Cr (III) & Fe (III) onto Chelex 100

Metal	$-\ln(1 - F) = kt$	$-\ln(1 - F^2) = kt$	$3 - 3(1 - F)^{2/3} - 2F = kt$
Chromium (III)	$K = 0.065$ [min ⁻¹]	$K = 0.049$ [min ⁻¹]	$K = 0.016$ [min ⁻¹]
	$R^2 = 0.979$	$R^2 = 0.973$	$R^2 = 0.983$
Iron (III)	$K = 0.087$ [min ⁻¹]	$K = 0.084$ [min ⁻¹]	$K = 0.015$ [min ⁻¹]
	$R^2 = 0.714$	$R^2 = 0.721$	$R^2 = 0.619$

F is the fractional approach to equilibrium all the above equations, where k is the corresponding rate constant. Results from the present investigation were shown in Table 2, and shows that the metal uptake by Chelex 100 resin is best fitted by the moving boundary controlled mechanism for Cr (III) and by the particle diffusion controlled mechanism for Fe (III).

Initial pH effect

One of the most important parameters affecting the extraction procedure is the pH of the solution, because the formation of soluble metal complexes and their stabilities in aqueous solutions are strongly related to the pH of the medium. The influences of pH on the retentions of Cr (III) and Fe (III) ions were examined. The results are given in Figure 5.

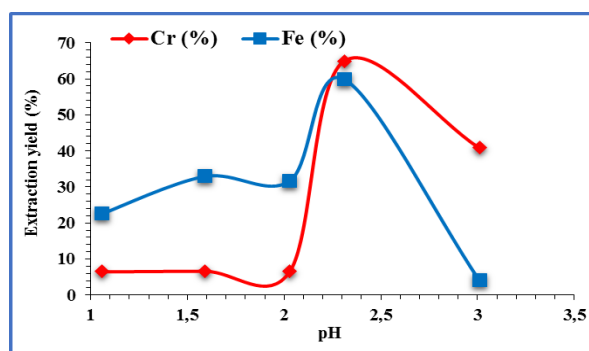


Figure 5. Effect of initial pH for efficient extraction of Cr (III) and Fe (III) using Chelex 100: $[Cr(III)] = [Fe(III)] = 500 \text{ mg}\cdot\text{L}^{-1}$, $T = 20 \pm 1 \text{ }^{\circ}\text{C}$, agitation speed = 500 rpm

The quantitative recovery values were obtained for Cr (III) and Fe (III) at the pH range 1.6 - 3.97, 64.94 and 59.9 % for Cr (III) and Fe (III) respectively. The extraction decreases strongly at pH equal to 3. This noticed can be attributed to the behavior of the cations Cr (III) and Fe (III) (appearance and/or disappearance of the species of Cr (III) and Fe (III) in aqueous phase) in different pH . The capacities of retentions increase from 1.10 to 11.60 $\text{mg}\cdot\text{g}^{-1}$ and from 1.94 to 6.95 $\text{mg}\cdot\text{g}^{-1}$ respectively. The separation between both metals is maximal at pH 3.0.

Effect of initial Chromium (III) and Iron (III) concentrations

The effect of the initial concentration of the mixture was studied by varying the initial concentrations of Cr (III) and Fe (III) between 100 and 500 ppm and by using 0.2 g of Chelex 100 resin. The agitation speed was maintained constant in 500 rpm as well as the time of agitation (45 min). The volume of mixture is taken equal to 10 mL. The complex Chelex 100- Cr (III) was given in the scheme from the Figure 6.

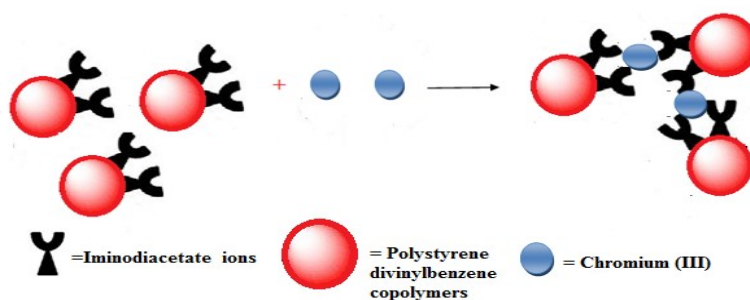


Figure 6. Schematic illustration of complex Chelex 100 - Cr^{3+}

The obtained results are presented as follows in the Figure 7 where from we notice that: in the first time, the iron reaches a maximum 87.3 % at 100 ppm then decreases until 59.9 %. On the other hand, for the chromium have a low increase between 100 - 450 ppm. It has been observed a strong increase which reaches a maximum 64.9 % at 500 ppm. The separation of both studied metals was maximal at 100 ppm.

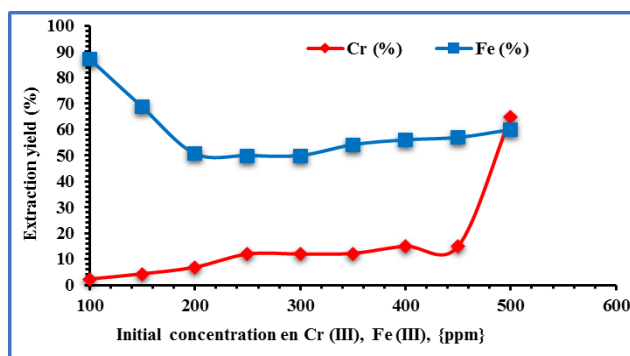


Figure 7. Effect of initial concentration of Cr (III) and Fe (III) using Chelex 100: $T = 20 \pm 1$ °C, agitation speed = 500 rpm and initial pH = 2.67

Thermodynamic studies

Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes are determined by using the equations 8, 9 and 10:

$$K_d = q_e / c_n \quad (8)$$

$$\Delta G = -RT \ln K_d \quad (9)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

where R [$8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$] is the ideal gas constant; T [K] is the absolute temperature and K_d is the thermodynamic equilibrium constant. The values of changes of enthalpy (ΔH) and entropy (ΔS) were calculated from the slopes and intercepts of the plot of $\ln K_d$ vs. $1/T$ by using equation (10) (shown in Figure 8) [17].

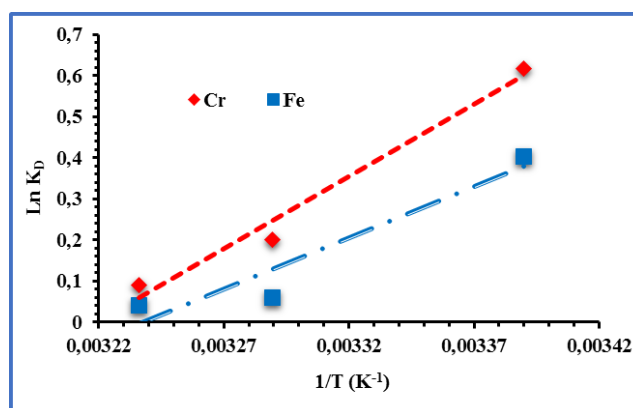
The relative parameters and correlation coefficient calculated from equations 8, 9 and 10 were listed in Table 3. The negative ΔG values show that, the sorption of ions of chromium and iron by Chelex 100 occurs spontaneously in 295 - 328 K while it is not appropriate in case of iron as indicated by the positive sign of ΔG at 309 K.

The enthalpy of the sorption, ΔH , is a measure of the energy barrier that must be overcome by reacting molecules [18]. The value of ΔH for sorption of Cr^{3+} and Fe^{3+} by Chelex 100 were negative, indicating that the extraction procedure of chromium and iron were exothermic nature of the extraction process of Cr (III) and Fe (III).

The negative value of entropy for two metals indicates the formation of a stable complex, which makes the extraction system more ordered resulting decrease in entropy value.

Table 3. Gibbs free energy, enthalpy and entropy changes for Cr (III) and Fe (III) extraction on Chelex 100

Metal	ΔH [kJ·mol ⁻¹]	ΔS [J·K ⁻¹]	ΔG [kJ·mol ⁻¹]·10 ³		
			295 K	304 K	309 K
Cr (III)	-29223.7	-94.0	-1.84	-0.63	-0.16
Fe (III)	-20735.1	-67.1	-0.93	-0.32	0.096

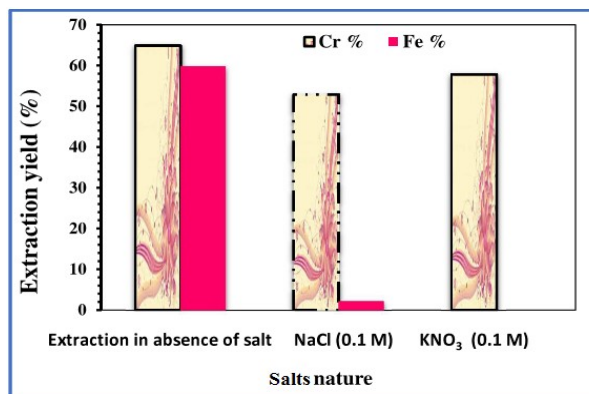
**Figure 8.** Evolution of $\ln K_D$ as function of $1/T$
[Cr (III)] = [Fe (III)] = 500 mg·L⁻¹, $T = 20 \pm 1$ °C, agitation speed = 500 rpm
and initial pH = 2.67

Effect of ionic strength

The effect of ionic strength on Cr (III) and Fe (III) extraction was studied by adding at the Chelex 100 resin NaCl and KNO₃ salts at 0.1 mol·L⁻¹ in the aqueous solutions.

The Figure 9 shows that the addition of two salts, in the concentration 0.1 M, chooses as this study have a negative effect on the extraction of Cr (III) and Fe (III) by the resin Chelex 100. So we notice that:

- the extraction yield of Cr (III) decreases from 64.94 to 52.96 % (extraction in absence of salt) and from 64.94 to 57.89 % during the addition of NaCl and KNO₃ respectively,
- the extraction yield of Fe (III) decreases strongly from 59.9 to 2.19 % and from 59.9 to 0 % during the addition of NaCl and KNO₃ respectively.

**Figure 9.** Effect of NaCl and KNO₃ salts concentration on the extraction yield:
[Cr (III)] = [Fe (III)] = 500 mg·L⁻¹, $T = 20 \pm 1$ °C, agitation speed = 500 rpm and

initial pH = 2.67

Also, the capacity of sorption of Cr (III) and Fe (III) decreases from 11.6 to 0.032 mg·g⁻¹ and from 6.95 to 0 mg·g⁻¹ respectively. The impact of considered salts, on the extraction of Cr (III) and Fe (III) was different according to the added salt and the negative effect for both metals follows the order: NaCl > KNO₃.

However, the impact of salts added to 0.1 M, on the separation of both metals follows the following decreasing order: KNO₃ (0 % of Fe (III)) > NaCl (2.2 % of Fe (III)).

Study of the elution

Once saturated in Cr (III) and Fe (III), the resin can be reused after elution of both metals, for the elution of Cr (III) and Fe (III) of our resin, we chose to test acids HNO₃ and HCl in concentrations equal to 0.5 M, 1 M and 2 M, and distilled water; 10 mL of eluent are added to 0.2 g of resin rich in Cr (III) and Fe (III), the mixture was shaken during 1 hour. After this time, we separate both phases and we measure the present metal in the aqueous phase. The yield on the elution was calculated by using the equation 11:

$$E(\%) = \frac{\text{Concentration of aqueous phase after elution}}{\text{Initial concentration of the mixture \{Cr(III), Fe(III)\}}} \quad (11)$$

The Figure 10 shows that the elution of the resin Chelex 100 by the solution of HNO₃ at 1 M is better than 0.5 and 2 M, the percentage of desorption was estimated to 57.6 % for both metals.

The elution of the resin Chelex 100 by the solution of HCl to 2 M was better than 0.5 M and 1 M, the percentages of desorption were: 36.3 and 42.1 % for the Cr (III) and Fe (III) respectively. The desorption of both metals by distilled water is unimportant {(Cr³⁺ was 0.308 %), (Fe³⁺ was 0 %)}.

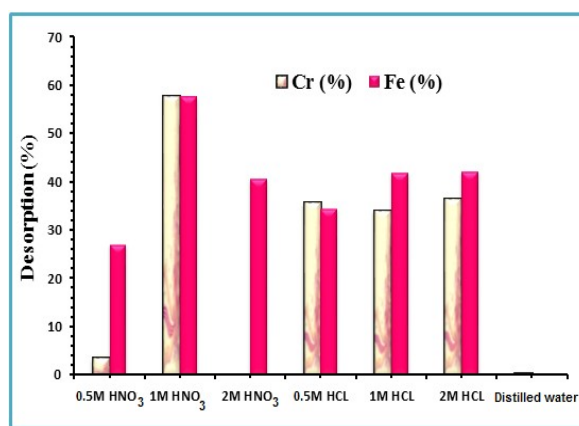


Figure 10. Desorption efficiencies of different eluent solutions for Cr (III) and Fe (III) removal from Chelex 100: $V = 10$ mL; $m = 0.2$ g; contact time = 60 min, $T = 20 \pm 1$ °C, agitation speed = 500 rpm

CONCLUSIONS

The Chelex 100 resin was tested on extraction and separation of Cr (III) and Fe (III) mixture. The efficiencies were determined as a function of various parameters such as the time, pH_i , mixture concentration, temperature and ionic strength effect. The results showed that the extraction yield and the extraction capacity of Cr (III) and Fe (III) by the resin Chelex 100 increased averagely in time. Equilibrium was reached after 45 and 5 min for Cr (III) and Fe (III) respectively. The pseudo second order kinetic model was most appropriate to describe the extraction process, the extraction capacity increases with increasing the initial concentration of Cr (III) and Fe (III). The thermodynamic study showed that the extraction process was exothermic and spontaneous.

The experimental results obtained showed that the separation of Cr (III) from Cr (III) and Fe (III) mixture was maximal at pH 3, initial concentration of Fe (III) 100 ppm and KNO_3 0.1 M.

The percentage of desorption was estimated to 57.6 % for both metals and 36.3 and 42.1 % for the Cr (III) and the Fe (III) by HNO_3 at 1 M and HCl solutions at 2 M respectively.

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