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Adsorption by liquid-solid extraction of mixture nickel (II) and copper (II) from aqueous solutions using chelating resin

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Abstract

Liquid-solid extractions (LSE) of Ni (II) and Cu (II) mixtures by Amberlite XAD-1180 resin were studied. The influence of operating parameters as equilibrium time (1 to 180 min) , the initial pH of aqueous solution (1.02 to 7.51) , effect of initial Nickel (II) and Copper (II) concentrations (10 to 100 ppm) , effect of temperature (293 to 328 K) and the effect of ionic strength (NaCl, KNO_3, Na_2CO_3) were investigated. The equilibrium time was 2 hours. The sorption capacity increases with the increase of the initial concentration of Ni (II) and Cu (II). Pseudo-first-order is more suitable for the sorption process for resin, and the adsorption of metals was described by the Langmuir isotherm. The effects of pH, concentrations, temperature, and ionic strength, were examined. It is found that these extractions are selective for Cu (II).

1. Introduction

Urbanization, industrial development, and heavy traffic lead to contamination of waters with heavy metals [1].

The extensive use of nickel (II) and copper (II) in metallurgy and other industries has resulted in the release of aqueous nickel and copper to the subsurface at numerous sites. Solvent extraction [2], membrane separation [3], adsorption [4], bioremediation [5], ion exchange [6], chemical precipitation [7], electrolysis [8], nano-filtration [9] etc. are the common techniques for removal and recovery of metals from industrial waste streams [10,11]. However, most of the preconcentration/separation methods used for this purpose have some disadvantages such as the requirement for large amount of toxic solvents, time consuming nature of the procedures, probability of sample contamination, very sensitive to operational conditions, employment of environmentally unsafe and expensive chemical products [12,13].

Among those approaches, solid phase extraction by chelating resins is commonly used [14-16]. The literature describes many chelating ion exchangers that were synthesized from XAD-2, XAD-4, XAD-7, XAD-16 and XAD-1180, copolymers that are suitable for metal ion separation and preconcentration from aqueous solution [11].

In this paper, was studied the optimization of nickel (II) and copper (II) mixture extraction by Amberlite XAD-1180 resin. Various parameters have been studied as contact time, the initial concentration of mixture Ni (II) and Cu (II), initial pH, temperature, and ion strength effect, to assess at the performance of Amberlite XAD-1180 resin.

2. Material and Methods

The Amberlite XAD-1180 resinalso possesses superior physical properties such as porosity (0.40-0.90cm^3/g), uniformdistribution of pore size (4 -9 mm), and high surface area (150-190 m^2/g).

A stock solution of 1 g.L^{-1} Cu (II) and Ni (II) ions were prepared by diluting an appropriate amount of $Cu(NO_3)_2.3H_2O$ and $Ni(NO_3)_2.6H_2O$ in distilled water. Other solutions of Cu (II) and Ni (II) 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.

The extraction of the metallic cations Ni (II) and Cu (II) was carried out under a mechanical agitation of 250 rpm, of which 0,4 g of the resin Amberlite XAD-1180 were put in contact with 20 mL of 100 ppm Ni(II) and Cu(II) mixture in erlenmeyer flasks. This step is necessary before any extraction to be able to determine a time, called the equilibrium time or the maximum extraction time.

The residual Ni (II) and Cu (II) concentrations in the aqueous solution after treatment were measured by Atomic Absorption Spectroscopy (AAS) -Perkin Elmer (PinAAcle 900 H), of Tlemcen University.

3. Results and discussion

3.1. Equilibrium time

This time is very important, it allowed us to know the time needed to dye the exchange balance between the two liquid phases [mixture (Ni (II)-Cu (II))] and solid [Amberlite resin XAD-1180]: Several prepared mixtures are brought into contact with the resin under mechanical agitation at 250 rpm, for varying periods of 1 to 180 minutes and at a concentration of 200 ppm in Ni (II) and Cu (II), after the separation of two phases, the quantity of metal cations remaining in the aqueous phase was determined using SAA. After calculating the different yields by the Eq.(1), Figure 1 shows the evolution of the yield as a function of the agitation time:

$$Y(\%) = \frac{C_0 - C}{C_0}.100 \qquad (1)$$

3.2. Agitation time effect

After calculating the different sorption capacities by the Eq.(2), Figure 2 shows the evolution of the two metals as a function of the agitation time**:**

$$q = \frac{C_0 - C_e}{m}.V \qquad (2)$$

The results found show that the maximum yields were (41.66%) and (93.26%) for Ni (II) and Cu (II) respectively, after 120 min of agitation. The yield increase (rapid sorption rate) of 1 to 120 min for Ni (II) and Cu (II) was due to the presence of a large number of active sites for the retention of free Ni (II) and Cu (II). A decrease in yield of 120 to 180 min due to the release of the Ni (II) and Cu (II) ions followed by a stabilization explained by the depletion of the Ni (II) and Cu (II). According to the results found, the sorption capacity of Cu (II) is greater than the sorption capacity of Ni (II) at equilibrium by the resin Amberlite XAD-1180, are 0.2523 and 0.4850 mg/g for Ni (II) and Cu (II) respectively.

Table 1: Effect of agitation time on sorption capacity of metal cations Ni (II) and Cu (II).

	Sorption capacity q (mg/g)	
Time (min)	Nickel (II)	Copper (II)
1	0.0070	0.0120
4	0.0240	0.0249
5	0.0180	0.0451
15	0.0860	0.2030
30	0.0410	0.2300
45	0.0280	0.3620
60	0.0435	0.4065
90	0.0630	0.4105
120	0.2523	0.4850

The two metals reach their maximum extraction after 120 minutes of agitation, we can conclude that:

- The retention of Cu (II) cation is more important than the retention of Ni (II) cation.
- The sorption capacity of Cu (II) is almost double the sorption capacity of Ni (II) (q (Cu (II)) ~2 q (Ni (II)).

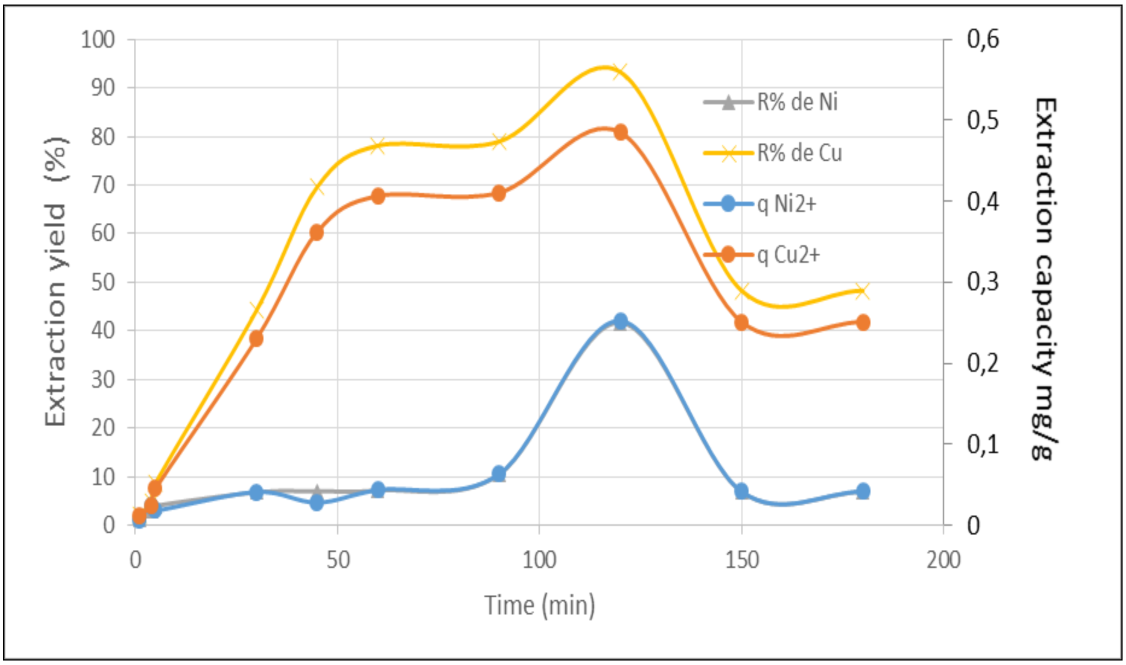

Figure 1: Effect of contact time on the ion exchange of Ni (II) and Cu (II) using Amberlite XAD-1180, V mixing = 20 mL, amount of resine = 0.4 g, [Ni (II)] =[Cu (II)] = 100 ppm, Agitation Rate = 250 rpm, pHi = 4.79, T = 20 ± 1 °C.

3.3 Kinetic models

To be able to examine the mechanism of the sorption process [17] of the Ni (II) and Cu (II) ions by the Amberlite XAD-1180 resin and to know which kinetic model is the most suitable for writing our experimental work, kinetic models should be tested:

- Pseudo-first order;
- Pseudo-second order;
- Intra-particulate diffusion.

Table 2: Main equations of kinetic models

Kinetic models	Rate equation	Integration (the linear form of the velocity equation)	The plot of the graph
		Main kinetic models	
Pseudo-first order (3)	$+\frac{dq_t}{q_t} = K_1(q_e - q_t)$	$Ln(q_e - q_t) = Ln\, q_e - K_1 t$	$Ln(q_e - q_t) = f(t)$
Pseudo-second order (4)	$+\frac{dq_t}{q_t} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t} = f(t)$
		Diffusion models	
Weber and Morris model (5)	$q_t = k_3 t^{\frac{1}{2}}$		$q_t = f\left(t^{\frac{1}{2}}\right)$

The different values of constants from the slopes and intercepts of linear plots of Eq.(3) (shown in Figure 2), Eq.(4) (shown in Figure 3), were summarized in Table 2.The results are shown in Tables 3 & 4. were: q_t (mg.g^{-1}) is the extraction capacity at the time of t; k_1 is the rate constant of the first order extraction (min^{-1}).k_2 is the rate constant of the second order extraction (g.mg^{-1}.min^{-1}).

Table3: Result of the application of Pseudo-first order model

	Ni (II)	**Cu (II)**
Concentrations (ppm)	100	100
k_1 (min^{-1})	0.0024	0.0239
coefficient of correlation	0.8425	0.9254
q_e calculated (mg/g)	0.2375	0.4669
q_e experimental (mg/g)	0.2523	0.4850

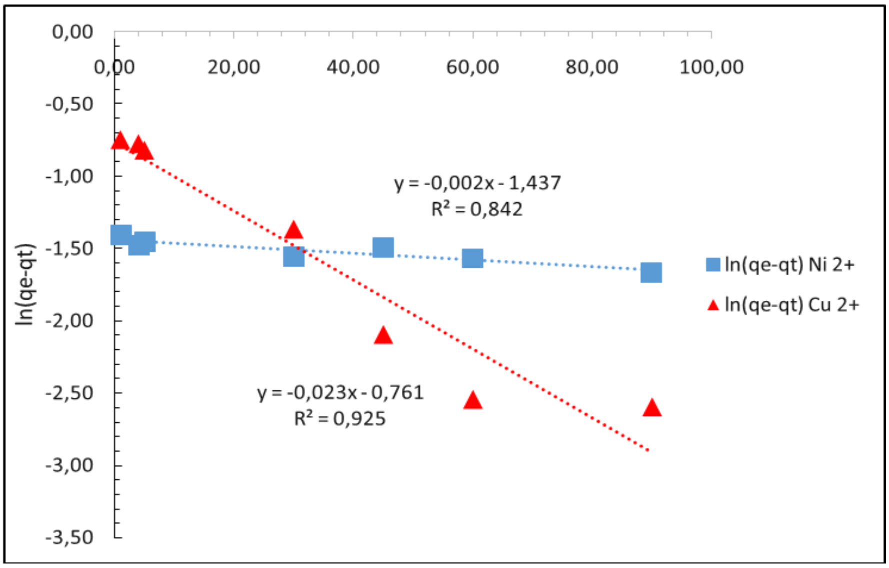

Figure 2: Lagergren plots for the extraction of Ni (II) and Cu (II) onto Amberlite XAD-1180. Amount of resin 0.4 g, volume of ion exchange medium 20 mL, T= 20±1°C, agitation speed250 rpm, initial pH 4.79 and initial concentration of Ni (II) & Cu (II) 100mg.L^{-1}

According to Table3&Figure 2, it is noted that: The application of this model shows that the theoretical (calculated) value of the equilibrium holding capacity of Ni (II) (q_e,cal (Ni(II)) equals 0.2375 mg/g, this value is close to the value of the retention capacity found experimentally (q_e, exp (Ni(II)) which equals 0.2523 mg/g, and with regard to the theoretical value (calculated) of the equilibrium retention capacity of Cu (II)) (q_e,cal (Cu(II)) equal to 0.4669 mg/g, this value is close to the value of the retention capacity found experimentally (q_e,exp (Cu(II)) which equals 0.4850 mg/g.

Table 4: Result of the application of Pseudo-second order model

	Nickel (II)	**Copper(II)**
Concentrations (ppm)	100	100
k_2 (min^{-1})	1.1700	0.0088
coefficient of correlation	0.7878	0.5751
q_e calculated (mg/g)	0.0587	1.0276
q_e experimental (mg/g)	0.2523	0.4850

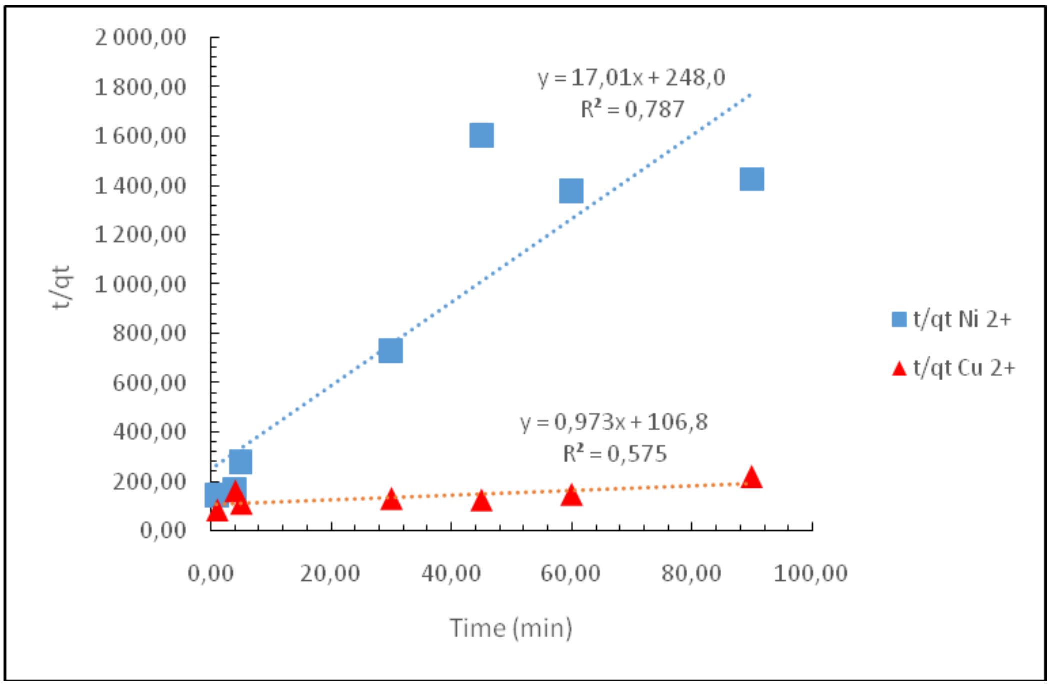

Figure 3: Pseudo second order kinetic model for the extraction of Ni (II) and Cu (II) onto Amberlite XAD-1180. Amount of resin 0.4 g, volume of ion exchange medium 20 mL, T= 20±1°C, agitation speed250 rpm, initial pH 4.79 and initial concentration of Ni (II) & Cu (II) 100 mg.L^{-1}

The application of this model shows that the retention capacities of Ni (II) and Cu (II) are very small with values of 0.0587 and 1.0276 mg/g respectively, these values are much lower than those found experimentally 0.2523 and 0.4850 mg/g respectively. Based on the application of these two kinetic models, It is concluded that the pseudo first order model is the most suitable for writing the extraction kinetics of the mixture (Ni (II) & Cu (II)) by the Amberlite resin XAD-1180, since the values of "q" are closer to those found experimentally as well as the correlation coefficients are higher.

3.4 Study of diffusion of Ni(II) and Cu(II)

Three possible extraction mechanism had been evaluated if the extraction of Ni(II) & Cu(II) into the resin must be considered as a liquid–solid phase reaction which includes diffusion of Ni(II) & Cu(II) 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 [18]:

(i) Film diffusion controlled process, the rate equation is:

$$-Ln(1-F)=kt \qquad (6)$$

(ii) Particle diffusion controlled process, with the equation as:

$$-Ln(1-F^2)=kt \qquad (7)$$

(iii) Moving boundary process:

$$3-3(1-F)^{2/3}-2F=kt \qquad (8)$$

Table 5: The regression coefficients and rate constants for the tested extraction mechanisms of Ni(II) &Cu(II)onto XAD -1180.

Metal	**-ln (1 - F)= k t**	**-ln (1-F^2) = k t**	**3 - 3(1 - F) $^{2/3}$- 2F= k t**
Ni(II)	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
Cu(II)	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. Table 5 shows that the process which dictates the rate of nickel (II) extraction is governed by the diffusion through the resin film, as opposed to copper (II), where the chemical reaction is the limiting factor.

3.5 Parametric study of the extraction of the mixture Ni (II) - Cu (II)

3.5.1 Effect of pH on the extraction of the mixture Ni (II) - Cu (II)

The study of the effect of the initial pH on the extraction of Ni (II) and Cu (II) by the resin Amberlite XAD-1180, is achieved by the pH change of 1.02 to 7.51.

- White precipitation and light blue coloration were noted prior to extraction with pH values of 7.04 and 7.51.
- After extraction, precipitation was noted for pH values greater than or equal to 6.01. The results are illustrated in Figure 4.

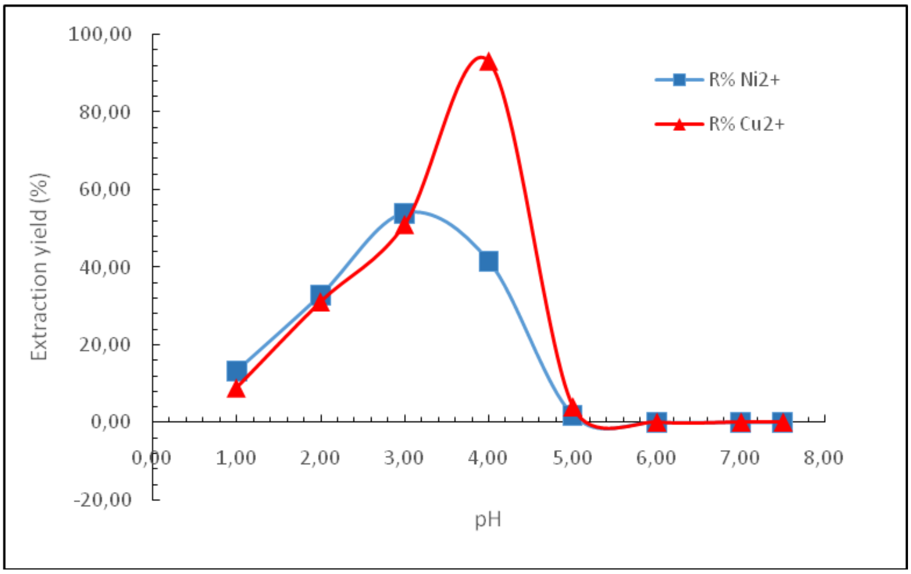

Figure 4: Effect of initial pH for efficient extraction of Ni (II)& Cu (II) using Amberlite XAD-1180. [Ni (II)]= [Cu (II)]= 100 mg.L^{-1}, T = 20 ± 1 °C, agitation speed 250 rpm

The results show that the yield reaches its maximum at pH equal to 2.99 and 4.02 with yields equal to 54.13 and 93.26% for Ni (II) and Cu (II) respectively.

- Part 1: pH 1.02 to 2.99 for Ni (II) and 1.02 to 4.02 for Cu (II) In these two intervals the yield increases rapidly to reach its maximum and since the solution is more concentrated in H_3O^+ ions, these ions created a challenge between them and the Ni (II)and Cu (II) ions, the predominance diagram (Figures 5 & 6) shows that at these pH values for the Ni (II)and Cu (II) respectively are in the form Ni (II)and Cu (II)free, these ions may be sorbed or adsorbed at a pH between [2,99-5,00] for Ni (II) and a pH between [4,02-7,51]for Cu (II), sorption of these ions is disadvantaged due to the protonation of active sites (appearance of the positive charge) on the resin.
- Part 2: pH of 5.00 to 7.51 for Ni (II) and Cu (II), we note that the yield has become null, the explanation is that at this interval we have a precipitation due to the appearance of new compounds:

* Precipitation of Nickel as Nickel hydroxide ($Ni(OH)_2aq$).
* Precipitation of copper as copper hydroxide ($Cu(OH)_2aq$).

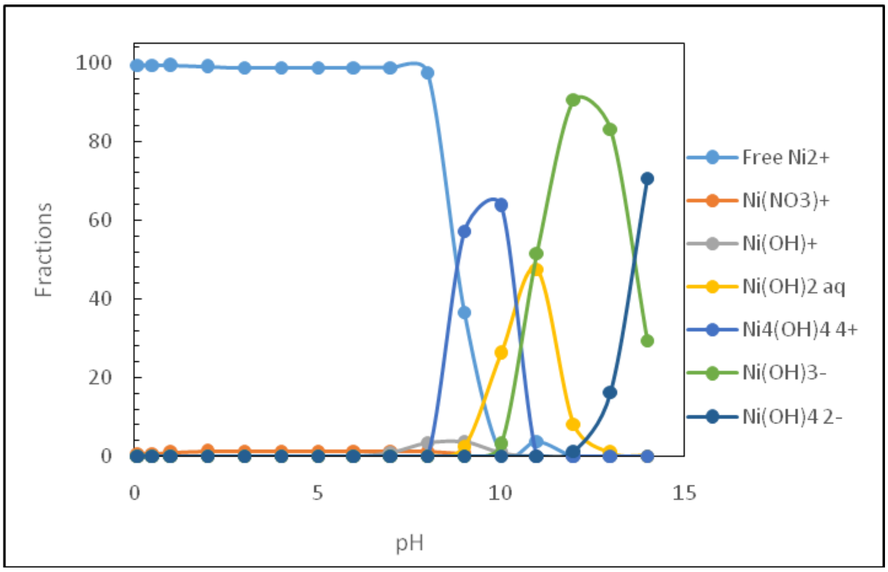

Figure 5: Predominance of Nickel in aqueous solution as function of pH (CHEAQS)[19].

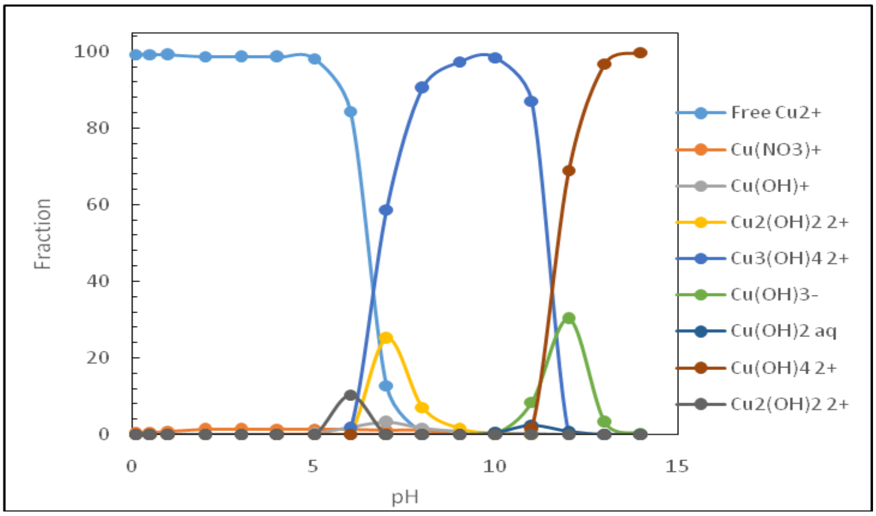

Figure 6: predominance of Copper in aqueous solution as function of pH (CHEAQS) [19]

The CHEAQS (Chemical Equilibria in Aquatic Systems) software helps us to study the metals present in the solution, by plotting the fraction of the metals according to the change in the pH of the medium. The variation in the pH of the medium plays a very important role in the predominance of the various nickel and copper species present in the aqueous solution.

3.5.2 Effect of the initial concentration of the mixture [Ni (II) - Cu (II)] at different concentrations

The study of this effect was carried out by the change in the initial concentration of the mixture [(Ni(II)-Cu(II)] 10 to 100 ppm, 20 mL of which is added to 0.4 g of Amberlite resin XAD-1180. All liquid and solid mixtures at different concentrations are subjected to mechanical agitation at 250 rpm, at room temperature and for a time equal to 2 hours. The results are illustrated in Figure 7.

Initially, the yield of Ni(II) was 46.31% and then increased slightly to 83.23% at 30 ppm. Yield stability was observed at 60 ppm, followed by a drop from 41.66 ppm to 100 ppm. However, for Cu(II), total extraction was 100% at 10 and 20 ppm, followed by a steady decrease to 100 ppm. The resin is more selective to Cu(II), which yields more than 100 ppm Ni(II).

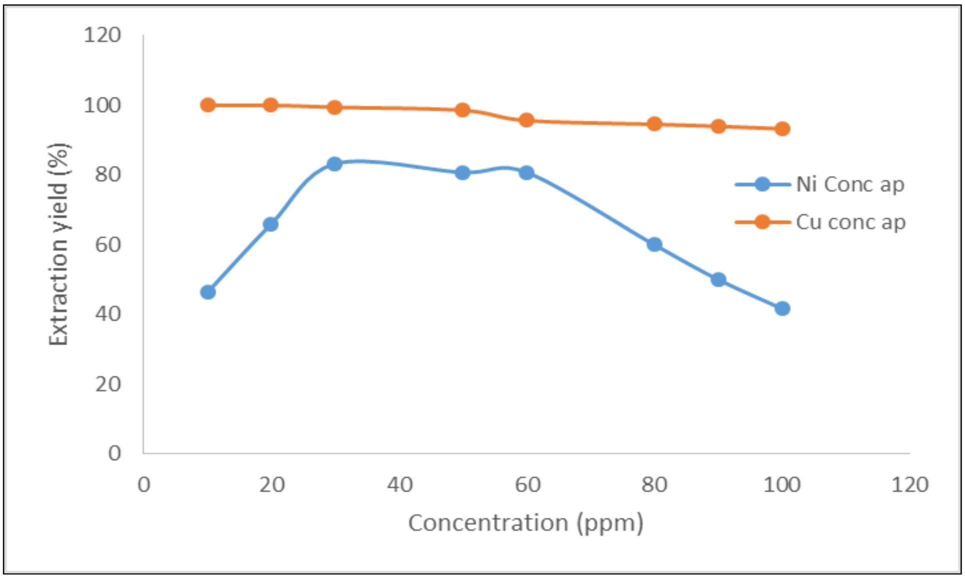

Figure7: Effect of initial concentration of Ni (II) and Cu (II) using Amberlite XAD-1180. T=20± 1 °C, agitation speed 250 rpm and initial pH 4.79

Isotherms were modeled with the two most commonly used equilibrium models, namely, Freundlich (Freundlich, 1906) (Eq. (9)) and Langmuir (Langmuir, 1918) (Eq. (10)), to evaluate which best fits the experimental data [20].

The Freundlich isotherm is an empirical equation used for non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption and is derived by assuming an exponentially decaying adsorption site energy distribution, which can be expressed as:

$$Lnq_e = Lnk_f + \frac{1}{n} LnC_e \qquad (9)$$

where k_f ((L/mg)) and n are the Freundlich constants denoting adsorption capacity and intensity of adsorption, respectively.

The Langmuir isotherm derived from simple mass action kinetics is based on the assumptions that molecules are adsorbed as a saturated monolayer of one molecule thickness with no transmigration in the plane of the surface, and interaction between adsorbed molecules are negligible with energy of adsorption remaining constant. The non-linear form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \qquad (10)$$

where q_m (mg/g) and b (L/mg) represent the maximum adsorption capacity and energy of adsorption (equilibrium constant), respectively [20].

Table 6: Modeled isotherm parameters for Nickel (II) and Copper (II) adsorption on Amberlite XAD-1180

		Metal	
	Parameter	Ni (II)	Cu (II)
Langmuir	q_m(mg/g)	3.2456	3.3266
	K_L (L/mg)	0.2293	0.6425
	R^2	0.9913	0.9948
Freundlich	1/n	0.2486	0.1933
	K_F (L/mg)	1.4716	1.6521
	R^2	0.8297	0.9778

Table. 6 shows that the isotherm of Langmuir better describes the adsorption of Ni(II) and Cu(II), this adsorption results from the complexation of ions with resin groupings, so the correlation coefficients are higher. The result found shows that the adsorption of ions takes place with the formation of a single layer with a single energy with no interaction between the adsorbed molecules.

3.5.3 Temperature effect

The application of the various temperatures 293, 298, 303, 308, 313, 318, 323, 328 K to the extraction of the mixture [Ni(II)-Cu(II)] was studied. The results are illustrated in Figure 8.

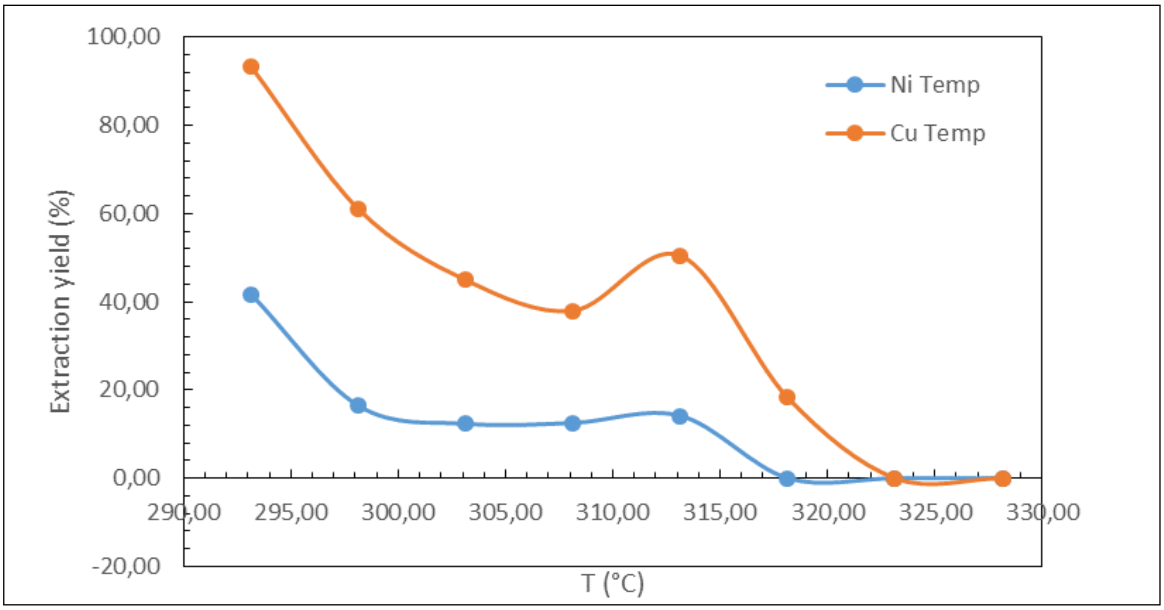

Figure 8: Effect of initial temperature of Ni (II) and Cu (II) using Amberlite XAD-1180. Agitation speed250 rpm and initial pH 4.79

This figure shows that the increase in temperature decreases the extraction efficiency from 41.668 to 0% and from 93.269 to 0% respectively for Ni (II) and Cu (II), which explains that by increasing temperature due to swelling of the banknotes which leads to an increase in size of the pores and cavities, and which makes the release of the ions Ni (II)and Cu (II) trapped in the resin easy. The separation between the two metals is maximal at 298 K. To be able to determine the different thermodynamic parameters (enthalpy: ΔH, entropy ΔS and free enthalpy ΔG), we trace Ln K_d according 1/T to which:

$$LnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (11)$$

This equation is derived from the following equations:

$$\Delta G = \Delta H - T\Delta S \qquad (12)$$

$$\Delta G = -RTLnK_d \qquad (13)$$

R: perfect gas constant (R=8.314 J.mol^{-1}.K^{-1}) k_d: distribution coefficient or partition coefficient of the two metals Ni(II) and Cu(II) between the two liquid and solid phases.
The plot of Ln K_d according to 1/T us has allowed us to determine and ΔHwhichΔS. $\Delta H/R$ and $\Delta S/R$ is the slope, and the ordinate at the origin respectively [21,22].

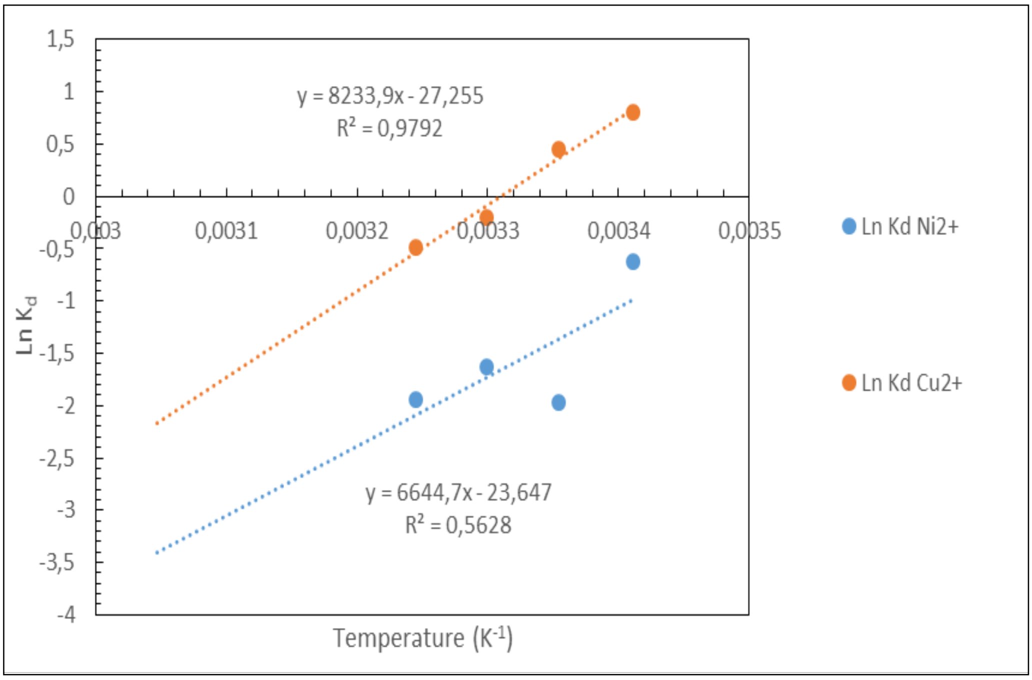

Figure 9: Evolution of Ln K_D as function of 1/T
T=20±1 °C, agitation speed 250 rpm and initial pH 4.79

Table 7: Thermodynamics parameters

	R^2	ΔH (KJ/mol)	ΔS (J/mol.K)	ΔG (KJ/mol)			
Temperature		-	-	293	298	303	308
Nickel(II)	0.5628	-55.24	-196.60	2.38	3.34	4.32	5.31
Copper(II)	0.9792	-68.45	-226.59	-2.05	-0.92	0.20	1.33

Table 7:

- ΔH<0 for both metals: exothermic process.
- ΔS<0 for both metals: decrease in molecular disorder.
- ΔG>0 for Nickel at all temperatures: non spontaneous process.
- ΔG<0 to 293 and 298 K for Copper: spontaneous process.
- ΔG>0 to 303 and 308 K for Copper: non spontaneous process.

3.5.4 Effect of ionic strength

The study of this effect is carried out by keeping the same operating conditions and adding the different salts (NaCl, KNO_3, Na_2CO_3) at different concentrations (from 0.1 to 2.5 M) in the aqueous phase. The results are illustrated in Figure 10.

The histograms obtainedshow that the addition of one of the three salts has a negative or positive effect on the extraction yield depending on the concentration of salt used.

❖ Effect of the addition of NaCl: Yield increases from 41.67 to 0.879 % and from 93.27 to 20.35 % respectively for Ni (II) and Cu (II), so there is a negative effect on the metal extraction efficiency.

❖ Effect of addition of KNO_3: Yield increases from 41.668 to 0% and from 93.27 to 8.75% respectively for Ni (II) and Cu (II), so there is a negative effect on the metal extraction efficiency.

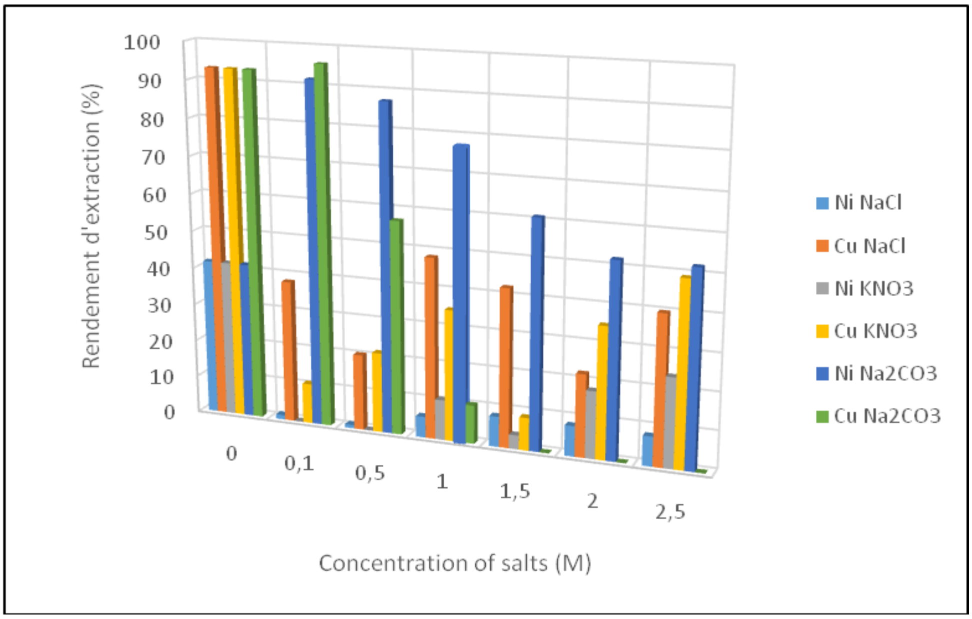

Figure 10: Effect of ionic strength of Ni (II) and Cu (II) using Amberlite XAD-1180. T=20±1 ◦C, agitation speed 250 rpm and initial pH 4.79

❖ Effect of the addition of Na_2CO_3: This salt has a positive effect on the extraction yield but with the smallest concentration from 41.668 to 91.758% and from 93.27 to 95.75% to 0.1 M in Na_2CO_3 respectively for Ni (II) and Cu (II), then it decreases with the increase in salt concentration until it reached 52.08% and 0% at 2.5 M in Na_2CO_3 for Ni (II) and Cu (II) respectively. In cases where the yield has decreased, it can be said that the aqueous phase has been enriched by cations from salts which make them easy to adsorb on the solid surface of the resin where they prevent the approximation of the metallic cations Ni(II) and Cu(II) by electrostatic repulsion, as well as active sites were stabilized by salt cations and therefore forces of attraction between the solid phase and the metallic cations Ni(II) and Cu(II) become weak, this phenomenon leads to a decrease in yield.

With regard to the increase in yield in the presence of Na_2CO_3 at 0.1 M, the presence of this salt in small quantities favours the extraction and facilitates the transport of the Ni (II) and Cu (II) ions.

4. Conclusions

The Amberlite XAD-1180 resin was tested on extraction of Ni (II) and Cu (II) mixture. The efficiencies were determined as a function of various parameters such as the time, pHi, mixture concentration, temperature and ionic strength effect. The results showed that the extraction yield and the extraction capacity of Ni (II) and Cu (II) by the resin Amberlite XAD-1180 increased averagely in time. Equilibrium was reached after 2 hours. The pseudo first order kinetic model was most appropriate to describe the extraction process, the extraction capacity increases with decreasing of the initial concentration of Ni (II) and Cu (II). The thermodynamic study showed that the extraction process was exothermic and not spontaneous.

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Conflict of interest: The authors declare that there is no any conflict of interest regarding the publication of this article.

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