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Heavy metals removal by ion-exchange resin: experimentation and optimization by custom designs

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ABSTRACT

The brassware workshops are part of the craft specialities of Fez (Morocco) city of, which generate toxic and harmful effluents. Indeed, the large quantity of effluents produced is rich in heavy metals. It is therefore necessary to treat them before returning them to the natural environment in order to respect the Moroccan discharge limits. In the brassware workshops, the manufacture of handcrafted parts goes through a chain of deposit and rinsing baths. These rinsing baths are loaded with heavy metals (copper, silver and nickel). The objective of this study is to study and evaluate the effectiveness of the cation resin Lewatit S 1568 in eliminating heavy metals (Cu(II), Ag(I) and Ni(II)). The influence of different parameters such as contact time, resin mass and stirring speed on the % removal of these metals is investigated. A custom design based on response surface methodology is used in this study to build predictive models and to optimize the reduction of heavy metals from brassware effluents by ion-exchange resin. Therefore, 21 sets of experiments are used. This method is developed to evaluate the effects of the process variables of removing the concentrations of the three heavy metals by cation resin exchange. The independent variables used in this process are (time (X_1), mass of resin (X_2) and stirring speed (X_3)) and their interaction in order to achieve optimal conditions are investigated. From the statistical analysis, the three models of heavy metals are found to be highly significant with very low probability values ($p < 0.0001$). The optimal conditions obtained are ($X_1 = 35.11$ min, $X_2 = 2.63$ g and $X_3 = 98.6$ rpm) with a total elimination of Cu(II) and Ni(II), while for silver ion Ag(I) the elimination achieved does not meet the standards. On the other hand, the results of the study are analysed analytically and graphically.

Keywords: Ion-exchange resin; Brassware wastewater; Heavy metals removal; Response surface methodology (RSM); Custom design (CD)

1. Introduction

Brassware is part of the emblematic heritage of the spiritual capital, a craft that has fascinated the inhabitants of the Idrisside city for a long time; artisanal pieces adorned all their occasions, as well as their daily lives, which make them an element engraved in the collective memory of the people of Fez, in particular, and Morocco, in general. The brassware activity consists of making shaped pieces of copper, brass, pewter or silver by hammering a sheet of metal for the manufacture of utilitarian and decorative objects. The manufacture of these items carried out by treatments in a series of depositing and rinsing baths, which poses a problem because they generate complex and

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highly charged effluents, in particular a mixture of heavy metals (Cu(II), Ag(I) and Ni(II)) which are very dangerous and harmful. The presence of these metals in water poses significant environmental problems, which require treatment before any discharge into the receiving environment. heavy metals are characterized by high mobility, relatively high chemical stability and carcinogenicity. As they are not degradable, they accumulate in the environment, making them one of the most dangerous contaminants in such systems and posing a risk to human health.

There are many processes which have been applied to remove heavy metals from water and wastewater including: precipitation [1], absorption [2], adsorption [3], nanofiltration (NF) [4], ultrafiltration (UF) [5], reverse osmosis (RO) [6], electrodialysis (ED) [7] and ion-exchange resins (IER) [8,9].

The ion-exchange is the process by which ions in a solution are adsorbed onto a material called IER to be replaced by an equivalent amount of other ions of the same polarity. The most IER applications are: nitrate removal from groundwater [10], water softening [11], removal of sulphate ions [12], removal of fluoride [13], treatment of wastewater loaded with heavy metals [14] and removal of heavy metals [15]. In that way, Demirbas et al. [16] have studied the adsorption of Cu(II), Zn(II), Ni(II), Pb(II) and Cd(II) from an aqueous solution on synthetic resin Amberlite IR-120 and the results showed that the adsorption of Zn(II) and Ni(II) was higher than other metal ions studied. A study by Pehlivan and Altun [17] focused on the removal of Pb(II), Cu(II), Zn(II), Cd(II) and Ni(II) ions by a Lewatit CNP 80 type IER (weakly acidic). The authors obtained the maximum removal about 98%–99% for Cu(II), Zn(II), Cd(II), Ni(II) and 95% for Pb(II) in the range of pH 7–9. In addition, Elshazly and Konsowa [18] worked on the removal of nickel ions from polluted nickel chloride wastewater using a cation exchange resin in a batch-stirred tank reactor. The effect of various parameters such as nickel(II) ion concentration, stirring speed and temperature on the mass transfer coefficient of the diffusion-controlled reaction between nickel ions and the resin was studied. The results revealed that the use of this technique is promising for the treatment of wastewater, since the removal of nickel ions reaches up to 88.5%. Samadi et al. [19] studied the elimination of copper ions by three types of synthetic IER: CSMA-M, CSMA-MO and CSMA-MB, and they eliminated 89.32%, 100% and 97.4% of copper ions respectively at pH = 8.

In the last decennium, the response surface methodology (RSM) is a useful tool for modeling and statistical design of experiments, which has been increasingly implemented in different applications [20,21]. RSM is a set of mathematical and statistical techniques based on the adjustment of a polynomial equation to experimental data. It can be well applied when a response or set of responses of interest is influenced by several variables and can also take into account interaction effects. Types of RSMs used in the literature to model the physicochemical process include Central Composite Design (CCD), Box–Behnken Design (BBD), User-Defined Design and Customized Historical Data Model [22].

Al-Rashdi et al. [4] using a commercial NF membrane (NF270) to removing heavy metal ions from feed concentration of 1,000 mg/L, at pH = 1.5 and transmembrane pressure (TMP) of 4 bar, removed 100% of copper(II), 99% of cadmium(II), 89% of manganese(II) and 74% of lead(II). However, since NF270 is a loose membrane, it failed to reject arsenic(III). Benalla et al. [7] studied the feasibility of ED in heavy metals removal from brassware effluents using ED. They showed that AXE/CMX couple of ion-exchange membranes allows, to remove 98%, 95% and 97% of copper(II), silver(I) and nickel(II) respectively. With the exception of Ag(I), ED has brought the concentrations of copper and nickel below discharge standards. Cavaco et al. [8] treated the removal of chromium from electroplating industry effluents by two IER (Diaion CR11 and Amberlite IRC86). Their results showed that both IER were effective in removing chromium(III) from aqueous solutions. As mentioned above, the effectiveness of IERs which are widely documented especially in the removal of heavy metals [9] encourages us to evaluate the effectiveness of IER in the treatment of wastewater from the brassware workshops of Fez, which is highly charged in metal ions. The objective of this study is to evaluate the effectiveness of a cationic resin (Lewatit S 1568) in the removal of heavy metals from the brassware effluents of the city of Fez, especially Cu(II), Ni(II) and Ag(I) ions. For this purpose, the influence of time, resin mass and stirring speed on ions rejection is studied. The optimization of the operation is carried out using the RSM model by minimizing the concentration of heavy metals. The obtained quadratic models are validated by analysis of variance (ANOVA).

2. Experimental

2.1. Procedures

Experimental trials are conducted by using the strong acidic cation exchange resin Lewatit S 1568, based on a styrene-divinylbenzene copolymer, in monodisperse form supplied by the company LANXESS Energizing Chemistry (Germany). Physical and chemical properties of Lewatit S 1568 are given in Table 1.

The brassware samples analysed were carefully collected in order to obtain the most representative sample possible. They are collected in polyethylene bottles and stored in a cooler and transported immediately to the laboratory.

Table 1
Characteristics of cation exchange resin Lewatit S 1568

Type	Strongly acidic cationic resin
Matrix	Cross-linked polystyrene
Functional group	Sulfonic acid
Structure	Gel
Apparent density	830 g/L
pH stability	0–14
Total capacity	Minimum 2 eq/L
Ionic form as shipped	Na^+
Coefficient of uniformity	Maximum 1.1
Product storage limit	Maximum 2 y

The tests are carried out with a stirring system whose rotation speed can vary between 0 and 200 rpm. It allows the simultaneous stirring of the liquid contained in a series of 6 beakers, each filled with 250 mL of the brassware effluent. Resin masses ranging from (1, 1.5, 2, 2.5, 3.5 and 4 g) with a rotation speed of (10, 15, 30, 60, 90 and 120 rpm) for different times (10, 20, 30, 40, 50 and 60 min) are tested. The mixture is filtered through a Whatman filter paper and the filtrate is analysed. Each procedure is repeated three times, the result reported the average of the three measurements.

Regeneration is carried out with a saturated NaCl solution. This regeneration did not change the exchange capacity of the resin.

In all tests, a conductivity meter (Inolab WTW) is used to measure the electrical conductivity (*E*) and temperature of the samples. A pH-meter (JENWAY 3510 pH-Meter) is used for measuring the pH of the solutions. Heavy metals concentrations are determined by the technique of inductively coupled plasma spectrometry ICP-OES (Perkin-Elmer Optima 8000). Whereas, Ca^{2+}, Mg^{2+} and K^+ are analysed by atomic absorption spectroscopy.

The ion removal *R* (%) is calculated using the following expression:

$$R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (1)$$

where C_0 and C_e are the initial and final concentration (mg/L) of the heavy metal ion solution, respectively.

2.2. RSM statistical analysis method

RSM is a statistical technique for determining and representing the cause-and-effect relationship between actual mean responses and input control variables. The main idea RSM is to use a set of experiments designed to obtain an optimal response [23]. In this study the RSM design based on custom design (CD) is used with 21 experiments imported on Design Expert software to evaluate the relationship between the three responses ([Cu^{2+}] (Y_1), [Ag^+] (Y_2), [Ni^{2+}] (Y_3)) and the independent variables (contact time (X_1), mass of resin (X_2) and stirring speed (X_3)), Table 2 shows the process variables used for this design of the experiment where three levels were retained for the three factors, in addition. The design matrix obtained after the application of CD is mentioned in Table 3, as well as to optimize the relevant conditions of the variables in order to predict the best values of the responses. The predicted response values (*Y*) are described by a second-order polynomial equation, in general its form is written as:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (2)$$

where *Y* is the predicted response; b_0 the constant coefficient, b_i the linear coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients; n the number of design variables, and x_i, x_j the coded levels of design variables. In order to validate the model, an analysis of variance (ANOVA) study of the model is performed.

Table 2
Variables used in the experiments and their levels

Variable	Coding	Levels		
		–1	0	+1
Contact time (min)	X_1	0	30	60
Mass of resin (g)	X_2	0	2.69	4
Stirring speed (t/min)	X_3	0	45.48	120

3. Results and discussion

3.1. Physico-chemical and metallic characteristics of brassware wastewater

The operations are performed on an effluent from the workshops of brassware in the city of Fez and the analytical results of the untreated water are presented in Table 4.

The physico-chemical and metallic analyses of the brassware effluents give an idea of the concentration of ions contained in the in the wastewater to be treated. Table 4 shows the analytical results for brassware effluents. Results on Table 4 reveal that the effluent is alkaline (pH = 11.09), has a temperature of 32°C and characterized by a high electric conductivity (7.38 mS/cm) and a high content of silver and nickel (16.35 and 33 mg/L, respectively). These contents of silver and nickel exceed largely the Moroccan discharge limit values. For copper, it should be noted that with a content of 3.26 mg/L meets the Moroccan standards.

3.2. Parameters influencing the removal of heavy metals

The treatment of brassware effluents is carried out using Lewatit S 1568 resin. The influence of operating parameters such as contact duration, stirring speed and resin mass is studied.

3.2.1. Effect of duration

The effect of contact duration with Lewatit S 1568 resin has been studied by taking 3 g of resin with 250 mL of brasseware sample in six beakers with a stirring speed of 45 rpm and the contact duration ranging from 10, 20, 30, 40, 50 to 60 min.

Fig. 1 shows the variation of electric conductivity and hardness as a function of contact time. Fig. 2a and b show the variation of the removal of Cu^{2+}, Ag^+, Ni^{2+} and Ca^{2+}, Mg^{2+}, K^+ as a function of contact duration.

According to the results obtained in Fig. 1, the electrical conductivity remains almost constant, which is due to the replacement of the ions eliminated by the counter-ion of the resin.

The captured ions (Ni^{2+}, Cu^{2+}, Ag^+) are replaced by counter ions (Na^+) which occupied the active sites of the resin after the regeneration step by a concentrated NaCl solution. However, the hardness decreases rapidly with increasing contact time in the interval from zero to 20 min, then a stationary phase is reached and a minimum hardness value of 0.97 meq/L is obtained for a contact time of 50 min.

Table 3
Design experimental data

Trail	X_1: contact time (min)	X_2: mass of resin (g)	X_3: stirring speed (rpm)	Y_1: [Cu^{2+}] (mg/L)	Y_2: [Ag^+] (mg/L)	Y_3: [Ni^{2+}] (mg/L)
1	0	3	45	3.26	16.35	33
2	10	3	45	0.867	14.51	9.029
3	20	3	45	0.189	14.49	1.355
4	30	3	45	0.158	14.09	1.119
5	40	3	45	0.017	14.03	0.615
6	50	3	45	0	14.03	0.419
7	60	3	45	0	13.86	0.193
8	30	0	45	3.26	16.35	33
9	30	1	45	2.60615	14.8151	27.71
10	30	1.5	45	2.02233	14.4183	23.28
11	30	2	45	1.51306	14.0518	16.7492
12	30	2.5	45	0.86226	13.83	9.10868
13	30	3.5	45	0.14	13.66	1.11
14	30	4	45	0.12	13.09	0.50772
15	30	3	0	3.26	16.35	33
16	30	3	10	1.11092	14.28	13.804
17	30	3	15	0.85931	14.16	9.98371
18	30	3	30	0.64139	14.01	3.93316
19	30	3	60	0.13	13.78	1
20	30	3	90	0.0966	13.56	0.98792
21	30	3	120	0.10559	13.32	0.66779

Table 4
Characteristics of untreated water

	Brassware effluent	Discharge limit values [24]
Temperature, °C	32	30
pH	11.09	6–9
E, mS/cm	7.38	2.7
Cu^{2+}, mg/L	3.26	4
Ag^+, mg/L	16.35	0.1
Ni^{2+}, mg/L	33	5
Ca^{2+}, mg/L	56.112	–
Mg^{2+}, mg/L	7.5	–
K^+, mg/L	185	–
Cl^-, mg/L	829.53	–
Hardness, meq/L	2.42	–
Total alkalinity, meq/L	36.45	–

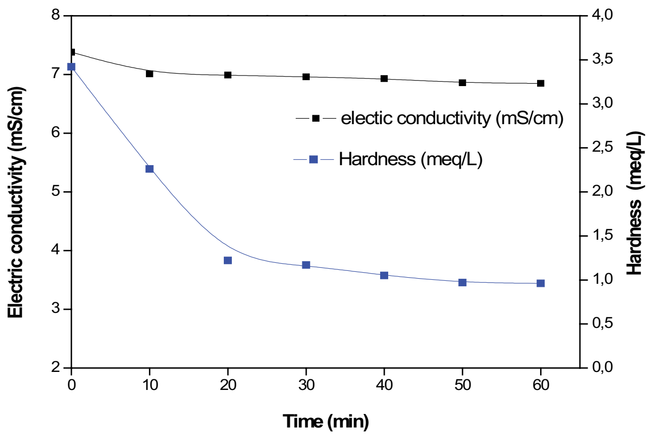


Fig. 1. Electric conductivity and hardness vs. contact duration.

Fig. 2a and b show the variation of the removal of Cu^{2+}, Ni^{2+}, Mg^{2+} and Ca^{2+} ions as a function of the contact duration. It can be observed that there are two phases: a fast phase where the is fast during the first twenty minutes, during this phase 98% of Cu^{2+}, Ni^{2+} and Mg^{2+} ions and 58% of Ca^{2+} are removed. Then comes a stationary phase in which, the quantities of removed ions are low. This can be explained during the first phase by the increase of the fixation of ions on the sites of the studied resin already occupied by Na^+ ions, whereas for the stationary phase, it is explained by the saturation of the fixation sites. Molecular diffusion of the ions takes place towards the surface sites of the resins until adsorption equilibrium is reached where all the sites are occupied. For monovalent ions, the removal of Ag^+ and K^+ ions increases slightly and tenfold with the contact duration. Removal of 15.22% and 48% are obtained for Ag^+ and K^+ ions respectively and for contact duration of 60 min. These low elimination rates are due to the competition with bivalent ions, which are more charged and rapidly occupy the active sites of the resins. The low elimination of Ag^+ is due to its charge, since it is a monovalent ion, the interactions generated with the charged sites of the resin, will be much weaker than those generated by bivalent and trivalent ions.

Removal of cations, follows the following order:

Cu^{2+} (100%) > Ni^{2+} (99.4) > Mg^{2+} (99%) > Ca^{2+} (66%) > K^{+} (48%) > Ag^{+} (15.22%).

The interaction of different cations at the active sites of the resin depends on ionic properties such as ion charge, electronegativity, ionic radius, and redox potential of these metals [25]. The selectivity of the tested resin can be explained by the charge and electronegativity of the ions. The most charged ions are the most attracted. On the other hand, for ions having the same charge, the electronegativity could explain the selectivity of the resin, which is consistent with the proposal of Allen and Brown [26], which stated that the more electronegative metal ions are more strongly attracted by the surface charge. The removal of Mg^{2+} ions is greater than Ca^{2+}, this is due to the concentration of Mg^{2+} is lower than that of Ca^{2+}. In addition the ionic radius of Mg^{2+} is smaller than that of Ca^{2+} which facilitates its access to the resin's active site.

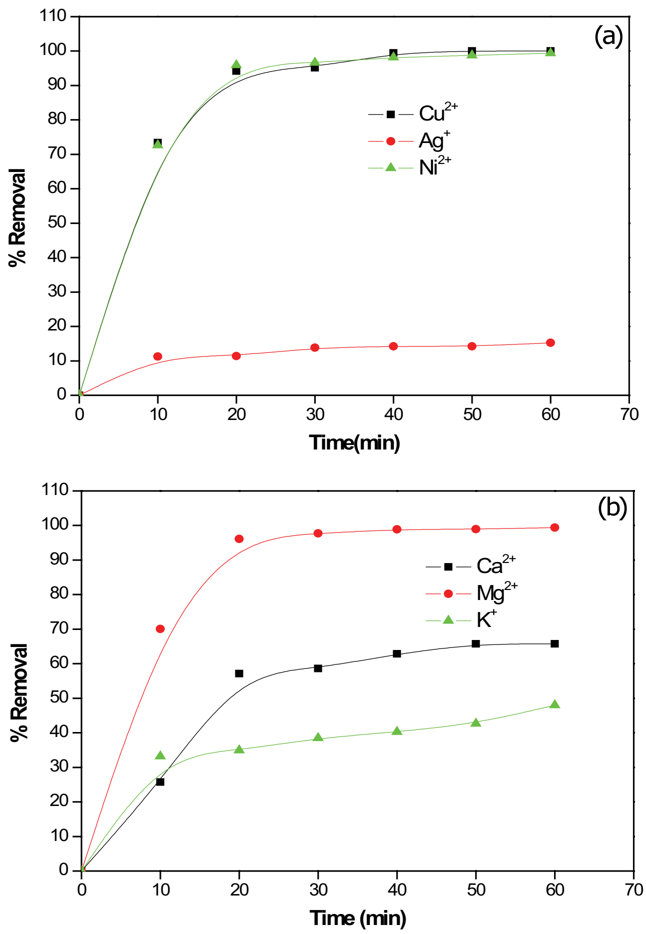


Fig. 2. Effect of contact duration on removal of Cu^{2+}, Ag^{+}, Ni^{2+} (a) and Ca^{2+}, Mg^{2+}, K^{+} (b) by IER.

3.2.2. Effect of resin mass

The resin amount is also one of the important parameters to obtain the quantitative absorption of metal ions. The sorption of metals ions is studied by varying the amount of Lewatit S 1568 (1–4 g), the stirring speed is fixed at 45 rpm during 30 min.

Fig. 3 shows the variation of electric conductivity and hardness as a function of mass of resin. Fig. 4 represents the variations of the removal of Cu^{2+}, Ag^{+}, Ni^{2+} and Ca^{2+}, Mg^{2+}, K^{+} as a function of resin dose.

As shown in Fig. 3, the electric conductivity remains almost constant. However, hardness decreases almost in linear way with increasing mass of resin.

Fig. 4a and b clearly show that the increase of the resin mass leads to an increase of the elimination of the studied cations. For Ca^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+} and K^{+} ions, the removal increases proportionally with mass resin. However, the increase of the mass resin leads to a gradual increase of the rejection of Mg^{2+} ions until a mass of 1.5 g, then a slight increase, announcing the saturation of the resin sites, is observed. In these conditions, removal of cations follows the following order:

Ni^{2+} (100%) > Cu^{2+} (99.4) > Mg^{2+} (99%) > Ca^{2+} (66%) > K^{+} (44%) > Ag^{+} (13%).

As the amount of resin increases, the removal of metal ions is also increasing. This result is expected because for a fixed initial concentration of metal ion, increasing the amount of resin will provide more surface area or ion-exchange sites and adsorption sites [27–29]. It is easy to understand that when the amount of resin increases, the number of available active sites also increases. It can be concluded that by increasing the adsorbent dosage, the removal efficiency is improved, but the ion-exchange density is reduced. The decrease in ion-exchange density can be attributed to the fact that a portion of the ion-exchange remains unsaturated during the process; whereas the number of available ion-exchange sites increases with increasing resin, resulting in an increase in removal efficiency [30].

3.2.3. Effect of stirring speed

In all the experiments dedicated to the influence of stirring speed, the volume of the brassware effluent is 250 mL, the resin mass is 3 g and contact duration is 30 min. The stirring speed is varying between 10 and 120 rpm. The result obtained is depicted in Fig. 5. Figs. 6a and 7b show the evolution of removal ions (Cu^{2+}, Ag^{+}, Ni^{2+} and Ca^{2+}, Mg^{2+}, K^{+}) as a function of stirring speed.

Fig. 5 shows that the electrical conductivity remains almost stable with the increase of stirring speed. However, the hardness drops sharply with stirring up to a speed of 30 rpm and then decreases in a linear way. This behaviour is due to the occupation of the Ca^{2+} and Mg^{2+} ions in the active sites of the resin.

Fig. 6a and b show the % removal of metal cations as a function of the stirring speed. Removal of Cu^{2+} and Ni^{2+} ions are significantly improved with the stirring speed. For only 60 rpm, 96% of these ions are removed. Unlike the removal of Ag^{+} ions, which does not exceed 18% even at

120 rpm. In the same way, removal of Mg^{2+} ions increases and reaches 85% at a stirring speed of 15 rpm. After this speed, a slight increase is observed until 60 rpm where a plateau is formed and the removal of magnesium reaches 98%. For Ca^{2+} ions, the elimination rate reaches 92% at a stirring speed of 120 rpm. On the other hand, the removal of K^+ ions increases up to a stirring speed of 30 rpm, thereafter a plateau is formed and the removal does not exceed 41% even at 120 rpm.

The effect of the stirring speed is well known, it facilitates the transport of the ions towards the surface of the resin and thus facilitates their diffusion towards the active sites. But, the selectivity of the resin with respect to the cation is managed by several parameters, namely the concentration, the electrical charge and the radii of the ions.

3.3. Optimization of operating parameters using the RSM method

ANOVA is a statistical technique that subdivides the total variation in a data set into items associated with specific sources of variation for the purpose of testing hypotheses about model parameters [31]. The results of the ANOVA are shown (Table 5) for the three models of heavy metal concentration (Cu^{2+}, Ag^+, Ni^{2+}) for the treatment of brassware by resin. From the *P*-values of the three models, it was possible to conclude that the developed model is highly significant at the probability level ($p < 0.0001$). In general, a *P*-value less than 0.0001 indicates that the model is significant, while values greater than 0.05 indicate that the model is not significant [20]. In addition, high values of the superior correlation coefficient ($R = 0.80$) are shown for all three models, which explains the good correlation between the experimental and predicted response values [32]. Regression analysis is used to generate the full quadratic model to predict the concentrations of heavy metals (Cu^{2+} (Y_1), Ag^+ (Y_2), Ni^{2+} (Y_3) in terms of the current factor is given:

$$Y_1 = -1.25207X_1 - 1.96262X_2 - 1.0002X_3 + 1.10951X_1^2 + 0.427095X_2^2 + 1.32831X_3^2 \quad (3)$$

$$Y_2 = -0.9525X_1 - 1.30895X_2 - 0.919086X_3 + 1.36445X_1^2 + 0.550991X_2^2 + 1.02231X_3^2 \quad (4)$$

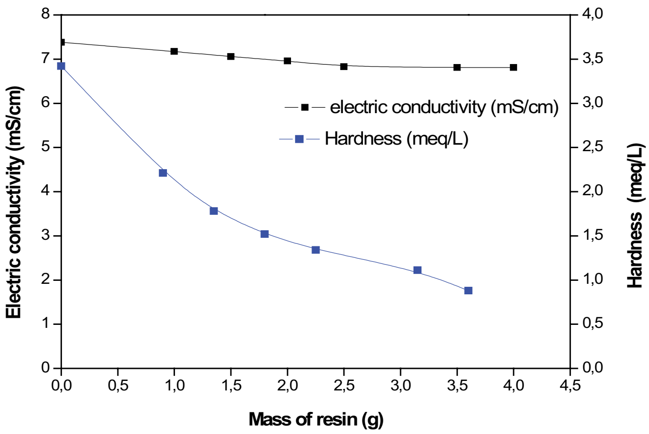


Fig. 3. Electric conductivity and hardness vs. mass of resin.

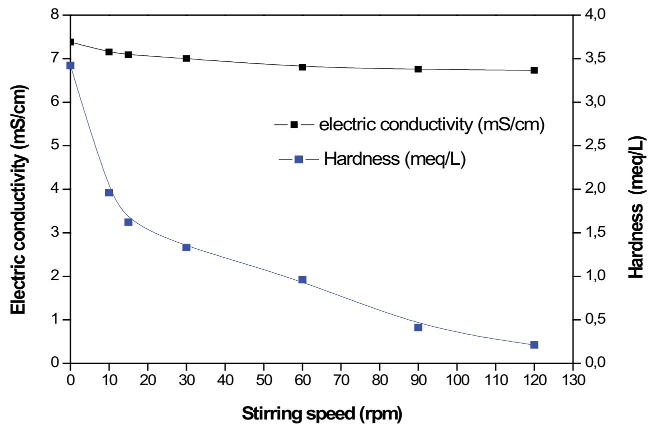


Fig. 5. Electric conductivity and hardness vs. stirring speed.

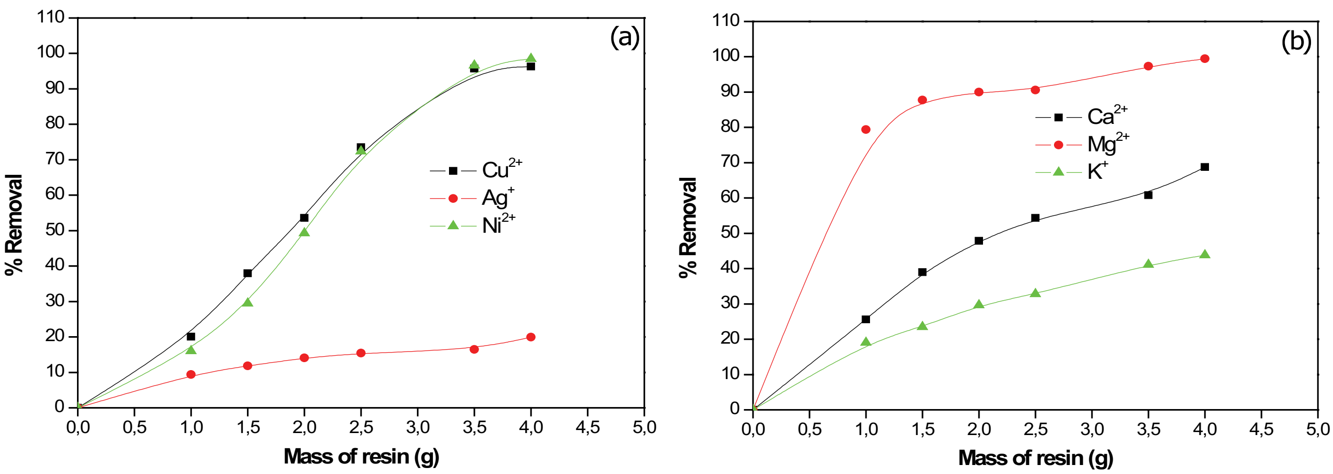


Fig. 4. Removal of Cu^{2+}, Ag^+, Ni^{2+} (a) and Ca^{2+}, Mg^{2+}, K^+ (b) vs. mass of resin.

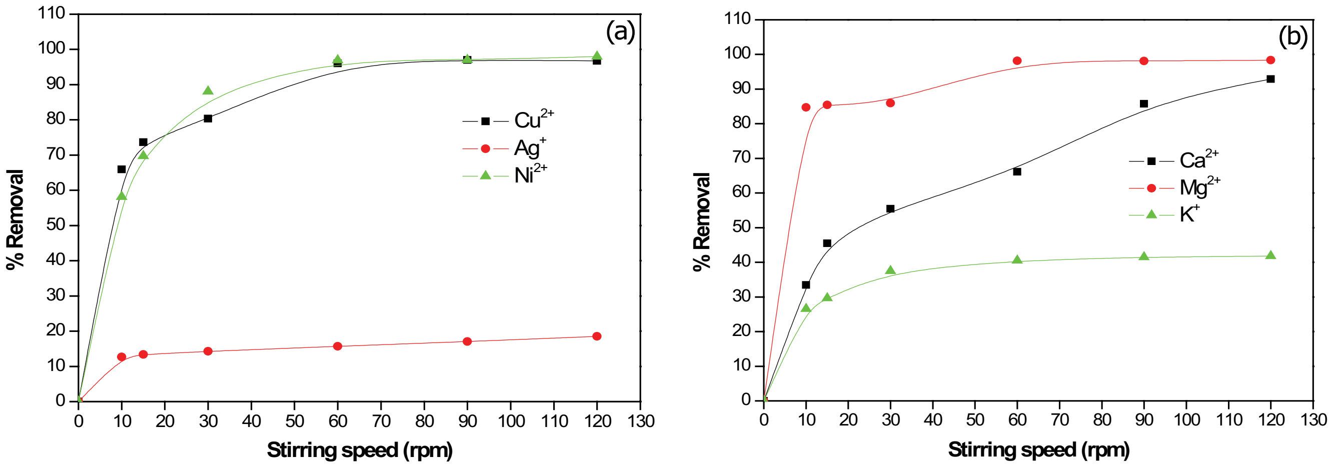


Fig. 6. Removal of Cu^{2+}, Ag^{+}, Ni^{2+} (a) and Ca^{2+}, Mg^{2+}, K^{+} (b) by Lewatit S 1568 resin vs. stirring speed.

Table 5
ANOVA for the quadratic model

Model	Sum of squares	dF	Mean square	*F*-value	*P*-value		R^2	R_{adj}
Cu^{2+}	23.65	6	3.940	13.87	<0.0001	Significant	0.856	0.794
X_1	4.88	1	4.88	17.17	0.0010			
X_2	13.84	1	13.84	48.71	<0.0001			
X_3	3.39	1	3.39	11.95	0.0039			
Residual	3.98	14	0.284					
Ag^{+}	14.15	6	2.360	10.27	<0.0001	Significant	0.812	0.735
X_1	2.82	1	2.82	12.29	0.0035			
X_2	6.16	1	6.16	26.81	<0.0001			
X_3	2.87	1	2.87	12.48	0.0033			
Residual	3.21	14	0.229					
Ni^{2+}	2,597.60	6	432.93	14.41	<0.0001	Significant	0.860	0.800
X_1	483.73	1	483.73	16.10	0.0013			
X_2	1,500	1	1,500	49	<0.0001			
X_3	390	1	390	13.0	0.0029			
Residual	420.75	14	30.05					

$$Y_3 = -12.4694X_1 - 20.9442X_2 - 10.7318X_3 + 11.2455X_1^2 + 2.74526X_2^2 + 13.8119X_3^2 \quad (5)$$

According to these equations, we can deduce that the three variables (contact time, mass of the resin, stirring speed) have negative effects on the response, since the regression coefficients associated with them are negative. A negative value indicates an inverse relationship between factor and response.

The actual and predicted tracing for each output response are shown in Fig. 7. These plots reveal that the values predicted by the model are in agreement with the experimental values for the range studied. In addition, the points are located closer to the diagonal line, which means that the errors are normally distributed and that the regression models fit the actual values quite well. Furthermore, on the basis of the high values of the regression coefficients offs obtained (Table 5) it can be said that the second-order model is adequate to represent the process of heavy metal removal by IER.

The predicted and experimental values are plotted, as shown in Fig. 7 for the three concentrations [Cu^{2+}], [Ag^{+}], [Ni^{2+}].

The response surface graphs (Fig. 8) of the effect of the interaction between the three parameters (time (X_1), mass of resin (X_2), stirring speed (X_3)) for the concentration of Cu^{2+}. The 3D response surface allows the interaction of these parameters to be visualized.

The response surface graphs (Fig. 9) of the effect of the interaction between the three parameters (time (X_1), mass of resin (X_2), stirring speed (X_3)) for the concentration of Ag^{+}, The 3D response surface allows the interaction of these parameters to be visualized.

The response surface graphs (Fig. 10) of the effect of the interaction between the three parameters (time (X_1),

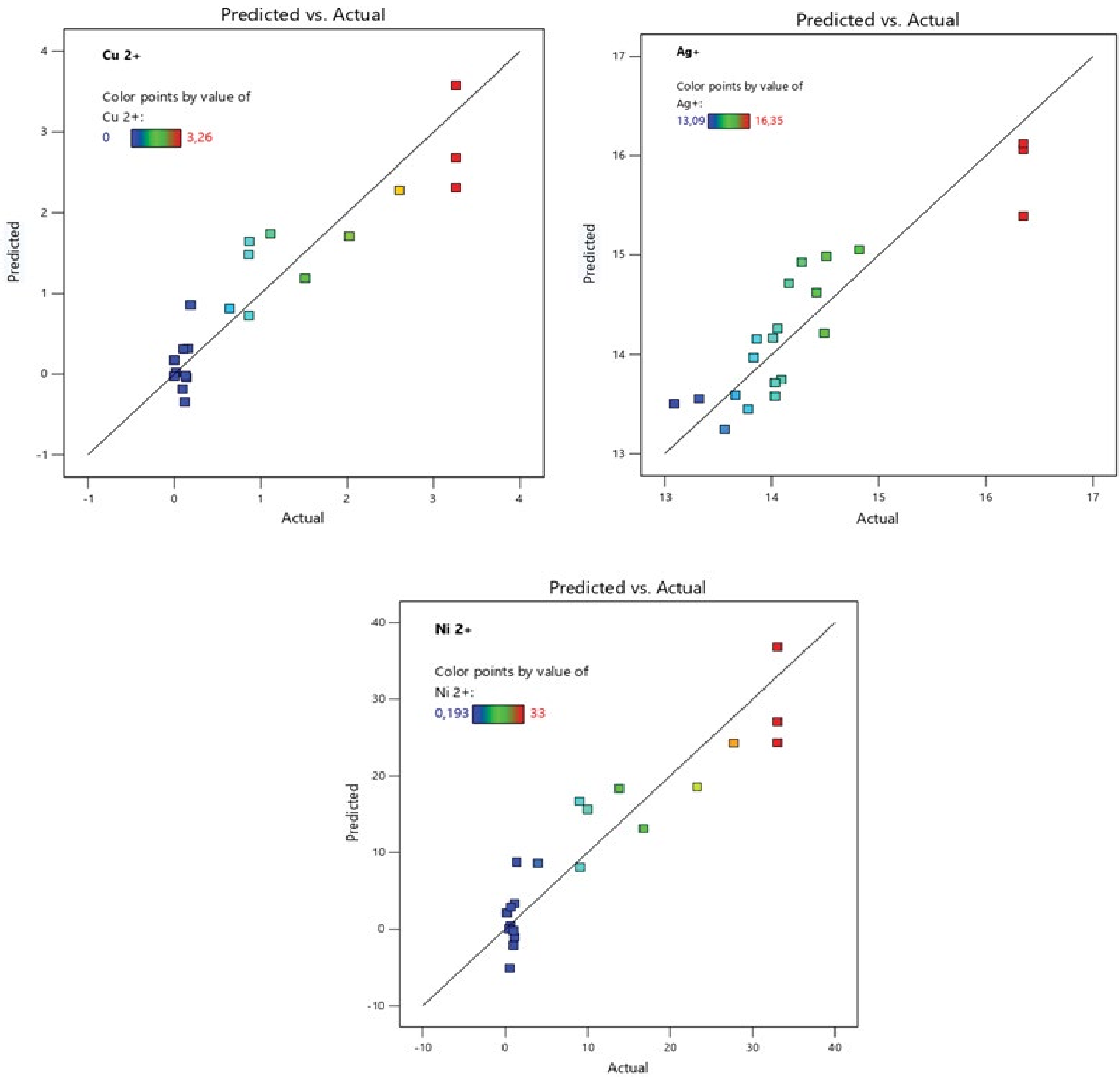


Fig. 7. Experimental data vs. predicted data of the responses ([Cu^{2+}], [Ag^{+}] and [Ni^{2+}]) calculated by applying the regression Eqs. (2)–(4).

mass of resin (X_2), stirring speed (X_3)) for the concentration of Ni^{2+}. The 3D response surface allows the interaction of these parameters to be visualized.

According to the ANOVA results, the most significant factor in the removal of the three ions (Cu^{2+}, Ag^{+} and Ni^{2+}) is the mass of resin followed by the contact time at the end of the circulation speed for X_1X_2 interaction showed the most significant effect, followed by X_2X_3 interaction for a fixed resin mass, while the effect of X_1X_3 interaction is shown minimum.

According to Figs. 8–10 the parameters X_1 and X_2 have a significant impact on the concentration of [Cu^{2+}], [Ni^{2+}] and [Ag^{+}] in the samples. The concentration in the samples is decreased at the highest limits of the factors X_1 and X_2. Moreover, the factor X_3 shows a linear effect on the lowering of the concentration of the abatement of Cu^{2+} and Ni^{2+} is complete over the entire range of factors studied, whereas the abatement of Ag^{+} does not allow to reach a content which agree with the standard limits.

3.4. RSM optimization

The process of removal of these heavy metals by resin ion-exchange wishes to use optimum parameters ((X_1), (X_2), (X_3)) as well as to obtain high efficiency in the removal of heavy metal in the brassware. Table 6 shows the optimal conditions of these studied. The conditions were found by minimizing the permeate concentrations of the three

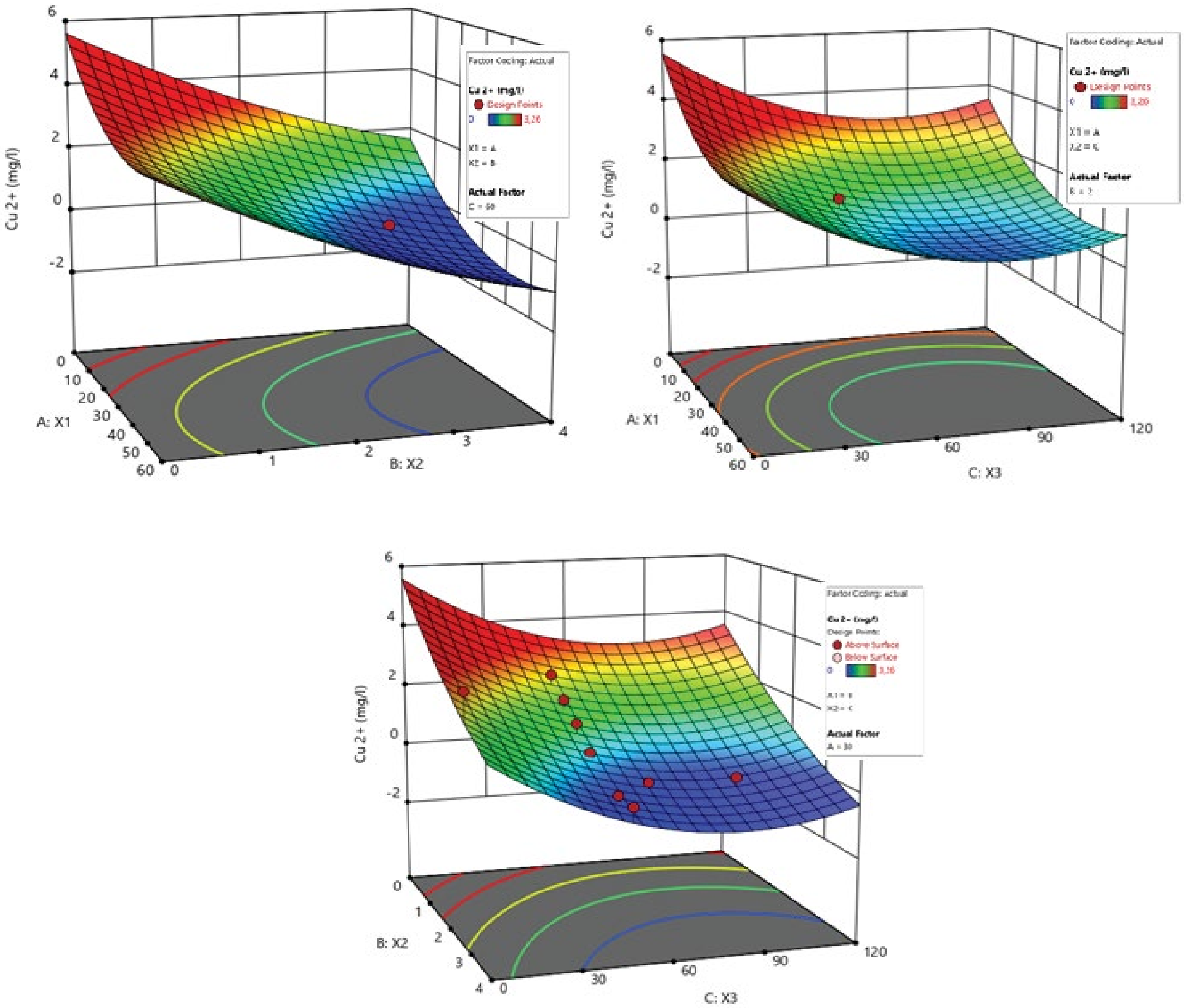


Fig. 8. 3D response surfaces of the effect of the interaction between the three parameters (time (X_1), mass of resin (X_2), stirring speed (X_3)) of concentration [Cu^{2+}].

heavy metals with a desirability function of 0.931. In fact, if the value of the desirability function is close to zero, the response is totally unacceptable, and if the value is close or equal to 1, the response is accepted [33]. These results accomplish the desired objective for divalent ions (Cu^{2+}, Ni^{2+}), while for the monovalent ion (Ag^+) its value remains above the standard norm. Table 7 shows the Characteristics of the treated water by IER, at optimal condition by RSM.

According to the results obtained, the physico-chemical quality of the treated water shows that IER is capable of bringing all the ion concentrations in the brassware effluents below the Moroccan discharge limit values. The only ion whose content has not been brought below the standards is silver. The explanation for this behavior is mainly due to the competition of silver ions with copper and nickel ions in the effluent, as silver is a monovalent cation, it is at a disadvantage compared to other bivalent ions. Therefore, other options have to be provided to bring the silver content down to the discharge limit values. Among these options, combining IER with ED or RO to reduce the silver ion concentration to the Moroccan discharge limit. There are other methods that can be coupled with resins to remove silver ions such as electrodialysis [34], activated carbon and reverse osmosis.

4. Conclusion

This work is dedicated to removal of heavy metals by cation exchange resins carried out on effluents from the brassware industry, namely the influence of contact time, resin mass and stirring speed on the % removal. The experimental results show that the percentage elimination of Cu^{2+}, Ni^{2+} and Ag^+ ions increases by increasing the dose of the resins, the contact time and the stirring speed and reaches important % elimination for the two metal ions Cu^{2+} and Ni^{2+} and respects the Moroccan discharge limit values, on the other hand for silver its concentration remains largely exceeding the discharge limit values and thus additional

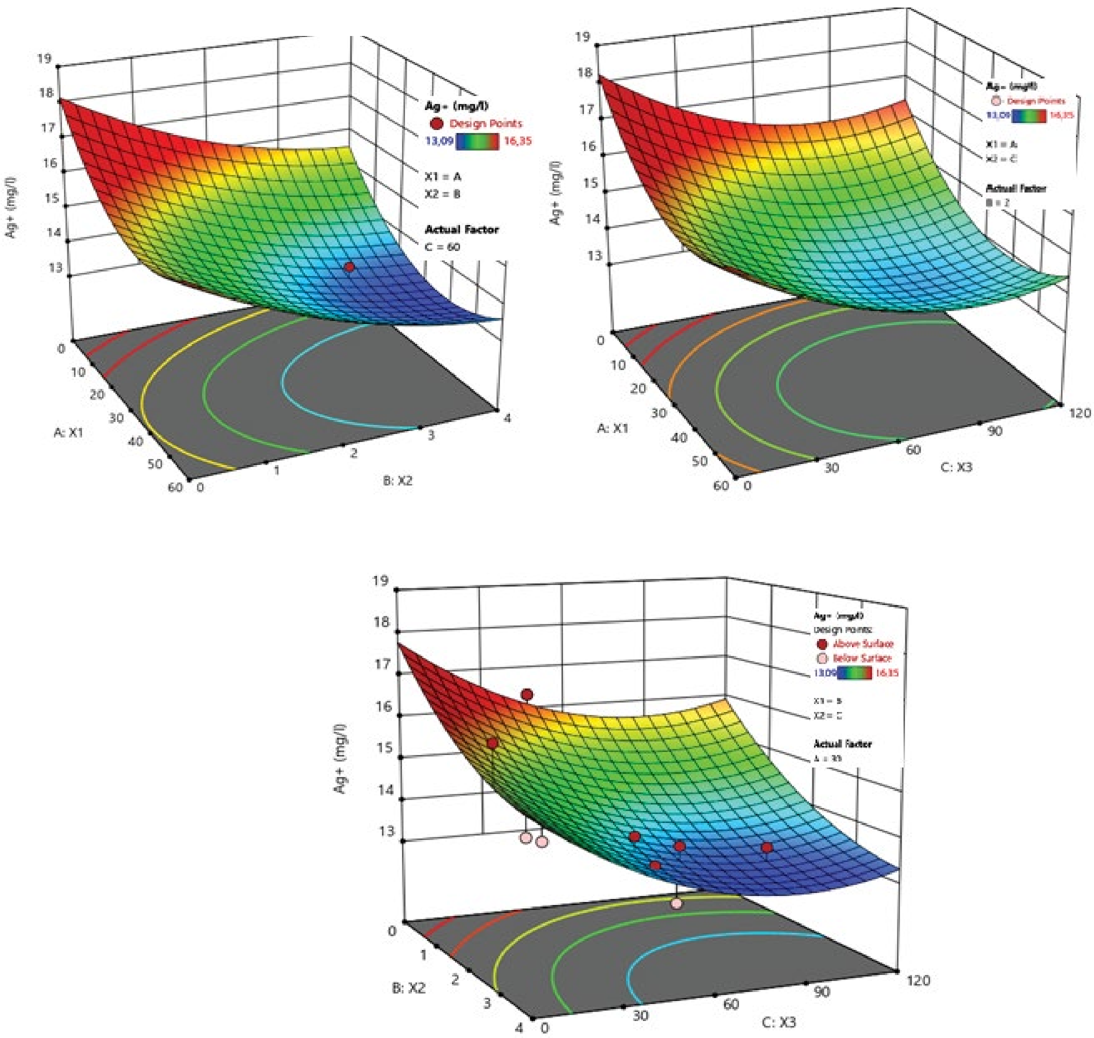
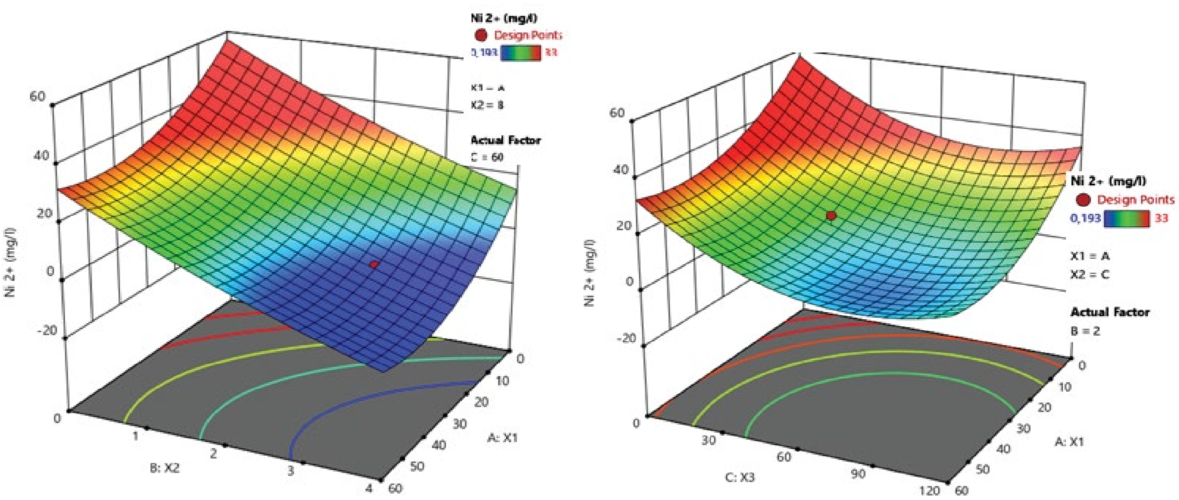


Fig. 9. 3D response surfaces of the effect of the interaction between the three parameters (time (X_1), mass of resin (X_2), stirring speed (X_3)) of concentration [Ag^+].



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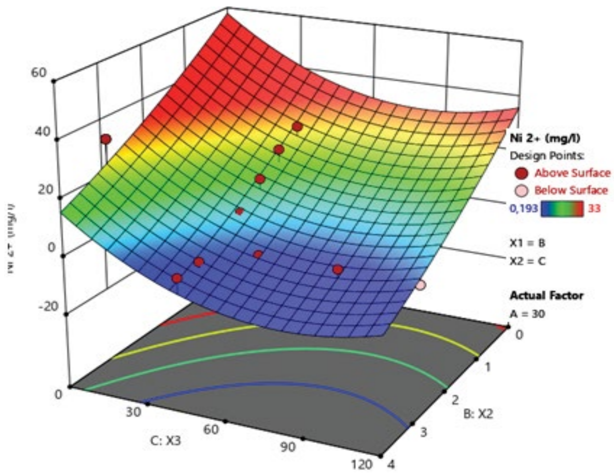

Fig. 10. 3D response surfaces of the effect of the interaction between the three parameters (time (X_1), mass of resin (X_2), stirring speed (X_3)) of concentration [Ni^{2+}].

Table 6
Response optimization by RSM

Time (min)	35.11
Mass of resin (g)	2.638
Speed of agitation (rpm)	98.600
[Cu^{2+}]	000
[Ag^{+}]	13.315
[Ni^{2+}]	0.193
Desirability	0.931

Table 7
Characteristics of the treated water by IER, at optimal condition by RSM

	Brassware effluent	Discharge limits values [24]
Temperature, °C	25	30
pH	10.7	6–9
E, mS/cm	6.72	2.7
Cu^{2+}, ppm	0.09	4
Ag^{+}, ppm	14.01	0.1
Ni^{2+}, ppm	0.33	5
Ca^{2+}, ppm	8	–
Mg^{2+}, ppm	0.7	–
K^{+}, ppm	108	–
Cl^{-}, ppm	726	–
Hardness, meq/L	0.45	–
Total alkalinity, meq/L	21.6	–

treatment is necessary in order to reduce the silver ion content and allow the treated water to respect the discharge limits.

The process of removing the three heavy metals by IER is optimized by RSM based on a custom design. According to the results, (Cu^{2+}, Ni^{2+}) have been removed almost completely, while for Ag^{+}, its value remains above the standard. Moreover, the ANOVA shows a reliability of the data with a good correlation coefficient R^2 exceeding 0.8 for the three heavy metals tested (Cu^{2+}, Ni^{2+} and Ag^{+}). The optimization of the models allows obtaining the optimal conditions at contact time, resin mass and stirring speed of 35.11 min, 2.638 and 98.6 rpm respectively.

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