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Optimization of conditions for Cu(II) adsorption on 110 resin from aqueous solutions using response surface methodology and its mechanism study

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ABSTRACT

An experimental study on removal of Cu(II) from aqueous solutions using 110 resins was carried out in a batch system. The effects of various operating parameters such as temperature, pH, and initial concentration were analyzed using response surface methodology (RSM). The results showed that the optimal adsorption condition of 110 resin for Cu(II) were 35℃, pH = 5.28, and initial Cu(II) concentration of 0.34 mg/mL. At optimum adsorption conditions, the adsorption capacity of Cu(II) was 336 mg/g, well in close agreement with the predicted value by the model. The apparent activation energy E_a and adsorption rate constant k_{298K} values were 11.80 kJ/mol and 3.92×10^{-5} s^{-1}, respectively. The adsorption isotherms data fitted well with the Langmuir model. Thermodynamic parameters (ΔG, ΔS, ΔH) suggested that the adsorption process was endothermic and spontaneous in nature. Desorption study revealed that Cu(II) can be eluted using 1.0 mol/L HCl solution, which indicated that Cu(II) in aqueous solution can be removed and recovered by 110 resin efficiently. Moreover, the characterization of the resin both before and after adsorption was undertaken using IR spectroscopic technique, scanning electron microscopy, and energy dispersive X-ray spectroscopy.

Keywords: 110 resin; Cu(II); Adsorption; Thermodynamic; Adsorption mechanism; Response surface methodology

1. Introduction

Separation of heavy metal ions from wastewater and drinking water is of great importance due to their toxic effects to living organisms [1,2]. Copper as one of the heavy metal metals, is widely used in many fields such as paints and pharmaceutical industry. Excess amount of copper entering both the water and the human body will cause serious environmental and public health problems [3–6]. Consequently, separation of the heavy metal ions from industrial effluents, various water resources and environment is very important.

Numerous research studies have been performed to develop methods to separate or remove heavy metals ions, including chemical precipitation [7], ion exchange [8], membrane separation [9], electrochemical deposition [10], and extraction chromatography [11]. Some common problems associated with these technologies have limited their industrial applications. For instance, the precipitation methods generate a large amount of sludge causing significant increase in

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treatment cost. The membrane system always has high treatment cost owing to the frequent change of membranes. In recent years, adsorption becomes a more promising method in environmental treatment technologies since it is applied to industrial effluents as an economic and effective technology for water purification [12–14]. And selection of an adsorbent is the key point for developing a proper adsorption technology as the specific type of adsorbent plays a dominant role in the adsorption process.

110 resin is a polymeric material which contains the functional group –COOH. Its principal characteristics are great chemical and physical stabilities, high exchange capacity, and good ability for regeneration. The adsorption process involves the variation of physicochemical parameters such as pH, temperature, initial metal concentration, and the reaction time. However, few studies have applied systematically statistical methods to investigate the combination of parameters that provides optimum adsorption conditions. RSM is proven to be an effective mean for the above mentioned purpose. It is a collection of statistical and mathematical techniques which has been successfully used for developing, improving, and optimizing process conditions. In this methodology, multivariate experiments are designed to reduce the number of assays necessary to optimize the process, as well as to collect data more precisely than univariate strategies. Therefore, it is less time consuming and more effective than any other conventional methods [15–19].

In this work, series of batch experiments were conducted to evaluate the capability of 110 resin for Cu(II) removal in aqueous solutions under various conditions. RSM was used to determine the optimization of adsorption conditions of Cu(II) on 110 resin with the combined effects of the key processing variables (temperature, initial pH, and initial Cu(II) concentration) on the desired response (adsorption capacity). In addition, further kinetics and thermodynamics of adsorption of Cu(II) on 110 resin were also investigated in this study. The resins were also characterized with IR spectroscopic technique, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) analysis. The experimental results may provide important information for the separation or removal of Cu(II) ion from aqueous solutions in the environment protection and wastewater treatment.

2. Materials and methods

2.1. Apparatus

IR spectra were obtained with Nicolet 380 FTIR; EDS spectra were obtained with INCA ENERGY 350 EDS. Cu(II) concentration was determined with Shimadzu UV-2550 UV–Visible spectrophotometer. Mettler Toledo delta 320 pH meter was used for pH measurement. The sample was shaken in the DSHZ-300A temperature constant shaking machines.

2.2. Materials

110 resin was supplied by Nankai University, China. And the properties were shown in Table 1. The standard stock solutions were prepared by dissolving an appropriate amount of $CuSO_4·5H_2O$. HAc–NaAc with pH 3–7 and $KOH–Na_2B_4O_7$ with pH 10.00 buffer solutions were prepared from the NaAc, HAc, $Na_2B_4O_7$, and KOH solutions. The chromophoric reagent of 0.1% 4-(2-pyridylazo)resorcinol (PAR) solution was obtained by dissolving 0.1000 g PAR powder into 100 mL 95% ethanol solution. All other chemicals were the analytic grade reagents.

2.3. Batch adsorption studies

Batch adsorption experiments were performed in the conical flasks containing 30 mL adsorption solution and 20.0 mg 110 resin. Adsorption of Cu(II) from aqueous solution to the adsorbents was studied at various pH values in the HAc–NaAc buffer system. Adsorption experiments were conducted in a shaker at 100 rpm at different temperatures (ranging from 15 to 35℃). The upper layer of clear solution was taken for analysis until adsorption equilibrium reached.

2.4. Experimental design for RSM study

RSM was used to optimize the adsorption conditions of 110 resin for Cu(II) from aqueous solutions. Factor combinations were obtained by the application of a Box–Behnken design (BBD) using software Design-Expert 7.1.6. In this study, the variables such as temperature, pH, and Cu(II) concentration are selected process parameters on the adsorption capacity of Cu(II) on 110 resin. The levels and independent variables are shown in Table 2.

Table 1
General description and properties of 110 resin

Items	Properties
Resin	Gel-type weak acid resin
Functional group	−COOH
Capacity/(mmol/ml)	≥ 12
Containing moisture (%)	70.0−80.0
Wet superficial density (g/mL)	0.70−0.80
True wet density (g/mL)	1.10−1.15

Table 2
Experimental design of the adsorption of 110 resin for Cu (II)

Symbols	Factors	Coded levels		
		−1	0	+1
A	Temperature (℃)	15	25	35
B	Initial pH	3	5	7
C	Initial Cu(II) concentration (mg/mL)	0.20	0.30	0.40

2.5. Analytical method

A solution containing a required amount of Cu(II) was added into a 25 mL colorimetric tube, and then 1 mL color reagent of 0.1% PAR-ethanol solution and 5 mL pH 10.00 KOH–$Na_2B_4O_7$ buffer solutions were added. After the addition of purified water to the mark of the colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 493 nm and compared with blank test. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following formulas:

$$Q = \frac{C_0 - C_e}{W} V \tag{1}$$

$$D = \frac{C_0 - C_e}{W \times C_e} V \tag{2}$$

where C_0 is initial concentration in solution (mg/mL), C_e is equilibrium concentration in solution (mg/mL), V is solution volume of solution (mL), and W is resin dry weight (g).

3. Results and discussion

3.1. Analysis of variance (ANOVA) and development of regression model equation

BBD was used to develop a correlation between the adsorption conditions and adsorption capacity of 110 resin for Cu(II). A total of 17 runs for optimizing the three individual parameters at the BBD were used to determine the experimental error. The ANOVA (Table 3) was investigating whether the process parameters have significant effects on the adsorption capacity, which indicates whether the model developed is meaningful. The determination coefficient ($R^2 = 0.9895$) and adjusted R^2 ($R^2_{adj} = 0.9798$) demonstrate adequacy of the model under the experimental condition. Moreover, the p-value < 0.05 suggests that model terms are significant. The lack-of-fit value (1.59) of the model implies nonsignificance, which is desirable. In this study, the linear coefficients (A, B, C), the quadratic term coefficient (A^2, B^2, C^2), and the interaction coefficient (AB, BC) were significant model terms. Adequate precision measures the signal-to-noise ratio and a ratio greater than 4 is desirable. The value of adequate precision ratio of 44.10 indicates adequate model discrimination [20].

From the discussion above, it is showed that the model has an adequate precision. To analyze the conversion rate, the following is the mathematical model in terms of coded factors developed by software Design-Expert 7.1.6:

$$\begin{aligned} y = {} & 309.60 + 35.75A + 15.50B + 11.00C + 7.50AB \\ & + 0.12AC - 17.50BC - 25.55A^2 - 61.05B^2 \\ & - 13.05C^2 \end{aligned} \tag{3}$$

3.2. The optimization of adsorption conditions

RSM was used to study the effects of the three factors on the adsorption capacity. The results of the adsorption capacity affected by temperature, pH, and initial Cu(II) concentration are showed in panels a, b, and c, respectively, of Fig 1. These types of plots show effects of two factors on the conversion rate and the other factor was kept at level zero. From the 3D response surface plots, the optimal values of the parameters could be observed, and the interaction between each parameter can be easily understood.

Fig. 1(a) indicated that adsorption capacity increased within the range temperature (15–35℃), which implies that the adsorption process is an endothermic process. The results show that adsorption capacity for Cu(II) increases rapidly with the increase in initial pH from 3 to 5.31 in the HAc–NaAc medium, and then decreased rapidly from 5.31 to 7 under the experimental conditions. At lower pH values, the Cu(II) ion uptake was inhibited in the acidic medium and this can be attributed to the presence of H^+ ion competing with the Cu(II) ion for the adsorption sites. Contrarily, the Cu(II) was prone to chemical precipitation at higher pH values.

Fig. 1(b) shows that the adsorption capacity increased from 220 to 320 mg/g with the increasing temperature and initial Cu(II) concentration. As see from Fig. 1(b), within the range of experimental variables, it appears that higher temperature and higher initial Cu(II) concentration have benefit to the adsorption capacity during the adsorption process, which is a significant effect on the adsorption capacity of Cu(II)

Table 3
ANOVA results of response surface quadratic model according to adsorption capacity of 110 resin for Cu(II)

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	Prob > *F*
Model	45481.83	9	5053.54	203.65	<0.0001
A	20604.50	1	20604.50	830.35	<0.0001
B	1922.00	1	1922.00	77.46	<0.0001
C	968.00	1	968.00	39.01	0.0004
AB	225.00	1	225.00	9.07	0.0194
BC	1225.00	1	1225.00	49.37	0.0002
A^2	2748.64	1	2748.64	110.77	<0.0001
B^2	1569.30	1	1569.30	632.42	<0.0001
C^2	717.06	1	717.06	28.90	0.0010
Residual	173.70	7	24.81		
Lack of fit	94.50	3	31.50	1.59	0.3243
Pure error	79.20	4	19.80		

R^2= 0.9895; R^2_{adj}= 0.9798; adequate precision = 44.10.

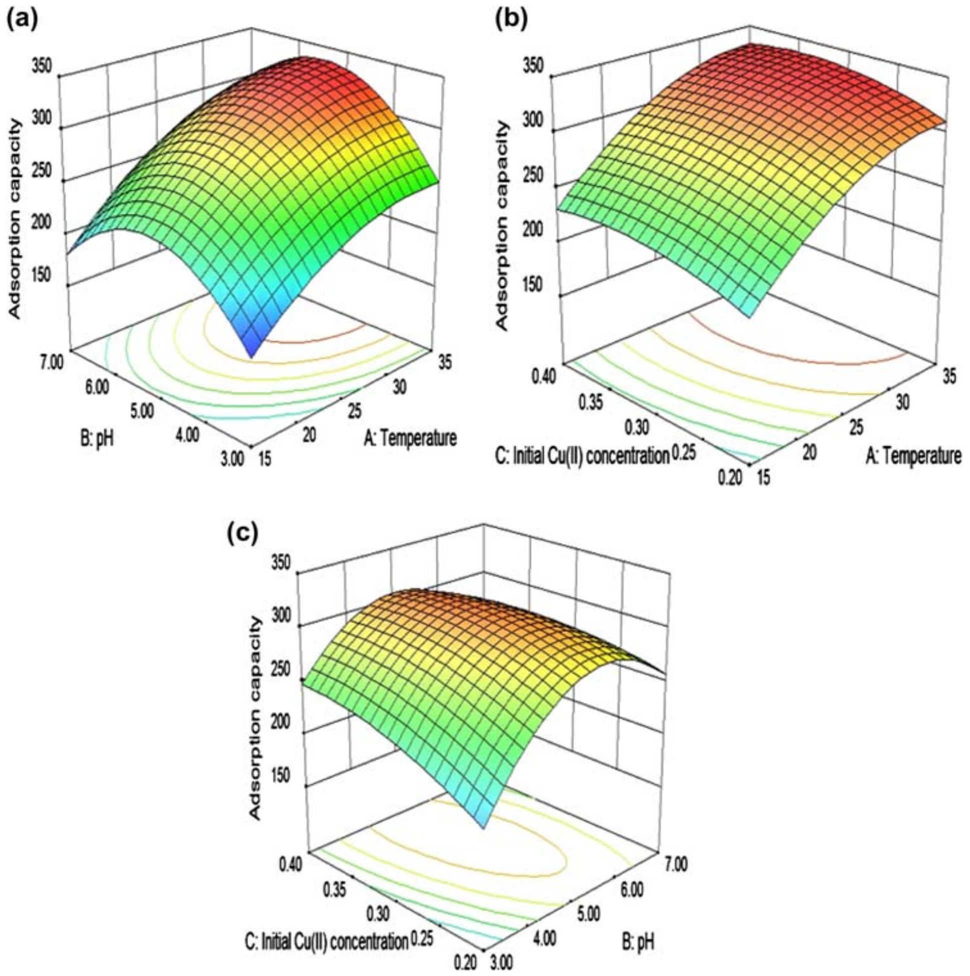

Fig. 1. Three-dimensional plots showing effects of (a) pH and temperature, (b) temperature and initial Cu(II) concentration, and (c) pH with initial Cu(II) concentration interactions on adsorption capacity of 110 resin for Cu(II).

on 110 resin. The possible reasons for this result are two aspects in the following: firstly, a higher temperature provides an important driving force to overcome mass transfer resistances of the Cu(II) between the aqueous and solid phases, thus increases the uptake; secondly, increasing initial Cu(II) concentration increases the number of collisions between Cu(II) ions and sorbent, which enhances the adsorption process.

Fig. 1(c) suggests that increasing the concentration of Cu(II) within the tested range was beneficial to the adsorption capacity for Cu(II) under the experimental conditions. In addition, increasing initial Cu(II) concentration increases the number of collisions between Cu(II) ions and sorbent, which enhances the adsorption process. When the initial Cu(II) concentration increased from 0.20 to 0.40 mg/mL, the adsorption capacity of 110 resin increased from 243 to 312 mg/g with pH values of 5.

The RSM-guided optimization demonstrated that the optimal adsorption conditions for Cu(II) on 110 resin from aqueous solutions are temperature of 35° C, pH of 5.28, and initial Cu(II) concentration of 0.34 mg/mL, and the predicted adsorption capacity reached 338 mg/g. Three batch experiments of the adsorption of 110 resin for Cu(II) were implemented using the predicted optimum condition in order to validate the developed mathematical models. The mean value of adsorption capacity was 336 mg/g, which obtained from real experiments which were in close agreement with the predicted value (338 mg/g) and much more than already reported in literature [21–23], indicating that the developed model was adequate for predicting the adsorption conditions of 110 resin for Cu(II) from aqueous solutions.

3.3. Determination of adsorption rate constant and apparent activation energy

Fig. 2. shows the adsorption kinetics of Cu(II) ions onto 110 resin. It is clear that the removal amount of metal ions increased rapidly during the few hours, and then increased slowly until the equilibrium state was reached within 15 h. A further increase in contact time had a negligible effect on the removal amount. The initial adsorption rate was very fast may be due to the existence of greater number of resin sites available for metal ions adsorption. As the remaining vacant surface sites decreasing, the adsorption rate slowed down due to formation of repulsive forces between the metals on the solid surface and in the liquid phase.

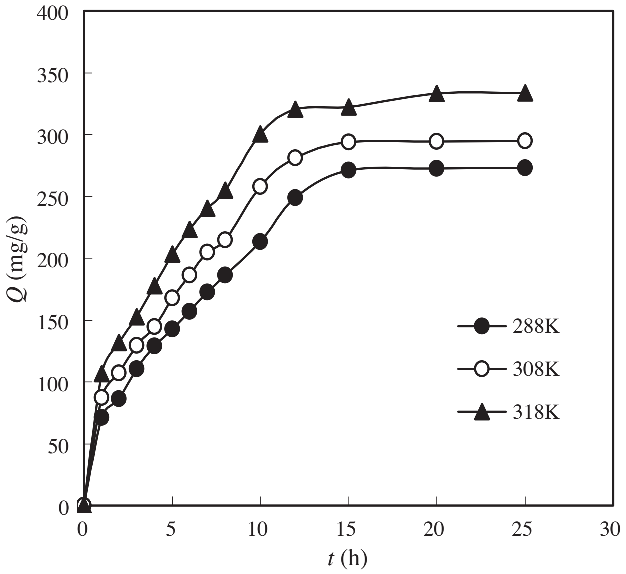

Fig. 2. Adsorption amount of different temperatures, resin 20.0 mg, $[Cu^{2+}]_0 = 0.34$ mg/mL, pH = 5.28, 100 rpm.

According to the Brykina method, the adsorption rate constant k can be calculated from:

$$-\ln(1-F) = kt \tag{4}$$

where $F = Q_t/Q_e$. Q_e (mg/g) and Q_t (mg/g) are the amounts of Cu(II) adsorbed at equilibrium and at any time t (h). The experimental results accord with the equation and a straight line was obtained by plotting $-\ln(1-F)$ vs. t (Fig. 3). It reveals good linearity as the R^2 is greater than 0.98 and the results are shown in Table 4, suggesting that the liquid film spreading was the predominating step of the adsorption process from the linear relationship of $-\ln(1-F)$ vs. t.

According to the formula of Arrhenius:

$$\lg k = -\frac{E_a}{2.303RT} + \lg A \tag{5}$$

where E_a is the Arrhenius activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to proceed, A is the Arrhenius factor, R is the gas constant (8.314 J/(mol K)), k is the adsorption rate constant, and T is the solution temperature.

The slope of straight line was made by plotting –lg k vs. $1/T$, and calculated by linear fitting, yields the apparent activation energy of $E_a = 11.80$ kJ/mol, which could be considered as a low-energy barrier in the adsorption process [24].

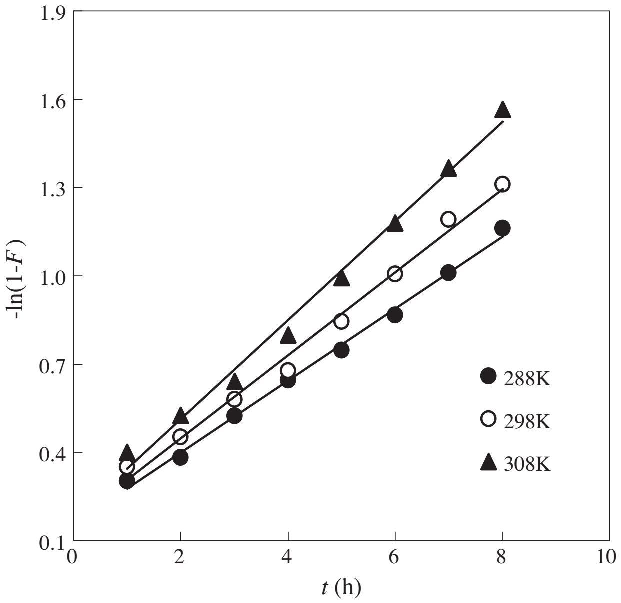

Fig. 3. Linear plots of $-\ln(1-F)$ vs. t by application of Brykina method.

3.4. Adsorption isotherms

Adsorption isotherms are quite important for explaining the adsorption process at equilibrium conditions. For example, the capacity of an adsorbent can be described by the adsorption isotherms, which can help us to understand the adsorption mechanism and provide an easier solution to further problems. In this work, the Langmuir and Freundlich isotherms are studied by varying the initial metal ions concentration in the range from 0.20 to 0.40 mg/mL with 20.0 mg 110 resin at pH 5.28, 100 rpm and temperatures 15, 25, and 35℃.

The Langmuir model is developed to describe the adsorption of an adsorbate on a homogeneous, flat surface of an adsorbent. The model assumes that each adsorptive site can only be occupied once in a one-on-one manner. The model can be written as follows:

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{6}$$

where Q_e is the equilibrium Cu(II) ions concentration on the adsorbent (mg/g), C_e is the equilibrium Cu(II) ions concentration in solution (mg/mL), Q_m is the maximal adsorption capacity of the metal ions on the adsorbent (mg/g), and K_L is the adsorption equilibrium constant (mL/mg) which reflects quantitatively the affinity between the 110 resin and Cu (II) ions. The plots of C_e/Q_e vs. C_e for the adsorption of Cu(II) ions onto resin give a straight line of slope $1/Q_m$ and intercept $1/Q_m K_L$. The Freundlich isotherm model, on the other hand, is used to describe the adsorption of an absorbate on a heterogeneous surface of an adsorbent. This model can be written as follows:

Freundlich isotherm:

$$\lg Q_e = \frac{1}{n} \lg C_e + \lg K_F \tag{7}$$

where K_F is the Freundlich constant and n is an empirical constant related to the magnitude of the adsorption driving force. One of the Freundlich constant, K_F, indicates the adsorption capacity of the adsorbent. The other Freundlich constant n is a measure of the deviation from the linearity of the adsorption.

The Langmuir and Freundlich parameters for the adsorption of Cu(II) ions are listed in Table 5. Evidently, both data-sets were fitted particularly well with the Langmuir model, as indicated by the R^2 values and the adsorption capacity values in Table 5. This suggests that the adsorption of Cu(II) ions by 110 resin is monolayer type and agrees with the observation that the metal ion adsorption from an aqueous solution usually forms a layer on the adsorbent surface. The increase in Q_m value with the temperature rise signifies that the process needs thermal energy (endothermic) and there was a chemical interaction between adsorbent and adsorbate [25].

3.5. Thermodynamic parameters

In any adsorption procedure, both energy and entropy considerations should be considered in order to determine what process will take place spontaneously. Values of thermodynamic parameters have the

Table 4
Isotherm constants for the adsorption of 110 resin for Cu(II) at various temperatures

T (℃)	Langmuir			Freundlich		
	Q_{max} ($mg\,g^{-1}$)	K_L ($mL\,mg^{-1}$)	R^2	n	K_F	R^2
15	314	15.64	0.9881	6.56	363	0.9438
25	340	19.99	0.9910	5.94	416	0.9585
35	378	24.09	0.9971	5.62	467	0.9769

Table 5
Adsorption rate constants (k) for the adsorption of 110 resin for Cu(II) and its correlation coefficient (R^2)

T (k)	Linearity relation of $-\ln(1-F)$ and t	$k \times 10^{-5}\,\mathrm{s}^{-1}$	R^2
288	$y = 0.1223x + 0.1545$	3.39	0.9958
298	$y = 0.1411x + 0.1668$	3.92	0.9912
308	$y = 0.1685x + 0.1761$	4.68	0.9918

great significance for practical application of a process. The amounts of Cu(II) ions adsorbed at equilibrium at different temperatures have been examined to obtain thermodynamic parameters for the adsorption system.

Thermodynamic parameters such as the Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process can be determined by using following equations [26] and reported in Table 6.

$$\lg D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

where D is distribution coefficient, R is the gas constant (8.314 J/(mol K), and T is the absolute temperature (K). A linear plot was obtained by plotting lg$D$ vs. $1/T \times 10^3$. The linear equation was $y = -0.4939x + 5.3672$ and the correlation coefficient was 0.998. As seen from Table 6, Gibb's free energy (ΔG) is negative, as expected for a spontaneous process, under the conditions applied and the decreasing of ΔG with increasing temperature indicated a better adsorption at higher temperatures. The positive value of entropy (ΔS) indicates the increasing randomness at the solid/liquid interface during the adsorption of Cu(II) ions on 110 resin. The positive value of enthalpy (ΔH) indicates the endothermic nature of adsorption process [27].

3.6. Elution test

To find out the optimum eluent and the optimum concentration of the eluent, 20.0 mg 110 resin adsorbed Cu(II) ions was separated and shaken with eluent until to equilibrium. The concentration of Cu(II) ions in aqueous phase was determined and then the percentage of elution was obtained. In practice, the use of resin for metal ions removal treatments is advantageous, however, in some specific cases, where metal ions completing agents may be present difficulties in elution. Because of this, different concentrations of HCl were employed in range from 0.5 to 3.0 mol/L and good results were obtained. The elution percentage is 96.4% with 0.5 mol/L HCl while it is all 100% with 1.0, 2.0, and 3.0 mol/L HCl. Considering the environmental pollution and resource waste, we choose the 1.0 mol/L HCl as the best elution.

Table 6
Thermodynamic parameters of 110 resin for Cu(II)

ΔH (kJ/mol)	ΔS (J/(K mol))	ΔG (kJ/mol)		
		$T = 288$ K	$T = 298$ K	$T = 308$ K
15.30	118.01	−18.68	−19.86	−20.42

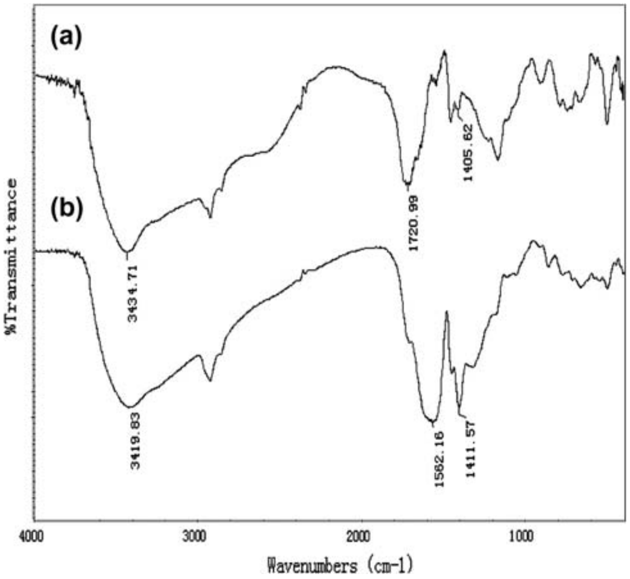

Fig. 4. IR spectra of 110 resin (a) before and (b) after loaded Cu(II).

3.7. Infrared spectra analysis

IR analysis is an important analytical technique for determination of adsorption mechanism. From the results above, it can be deduced that the adsorption of Cu(II) by 110 resin belongs to a chemical adsorption. Therefore, the functional groups of 110 resin C=O, C–OH, and Cu(II) are supposed to form chemical bonds. To identify the possibility of Cu(II) bonding to resin, IR spectra were obtained for 110 resin before and after Cu(II) adsorption, as shown in Fig. 4. In general, it is observed that there are significant changes in the IR spectra of 110 resin before and after Cu(II) adsorption. It should be noticed that the band at 3434 cm^{-1} is stretching vibrations of the surface hydroxyl groups, 1720 cm^{-1} and 1562 cm^{-1} is an indication of C=O [28]. The bands at 1405 cm^{-1} and 1411 cm^{-1} are assigned to the peak of the bond C-OH. It was found that the characteristic absorption peak of the bond C=O (1720 cm^{-1}) weakened after Cu(II) adsorption, and the new peak 1562 cm^{-1} was formed. The characteristic peak of the bond C-OH shifts from 1405 cm^{-1} to 1411 cm^{-1}. These results show that there are coordination bonds between oxygen atoms and Cu(II) and that H of C-OH has been exchanged with the formation of a complex compound [29]. These results revealed that the C=O groups participate in the adsorption process.

3.8. SEM and EDS analysis

After adsorption of as-prepared resin with Cu(II) solution, their color changed a little and the resin was studied by microscopic techniques (Fig. 5). The studies performed by means of optical microscope also confirm that the 110 resin has no pores in-house in the dry condition. The surface structure of resin was shown as SEM micrographs. And comparing the surface of 110 resin with Cu(II)-loaded resin, the smooth surface of the 110 resins turned thicker and coarser with granular flake material.

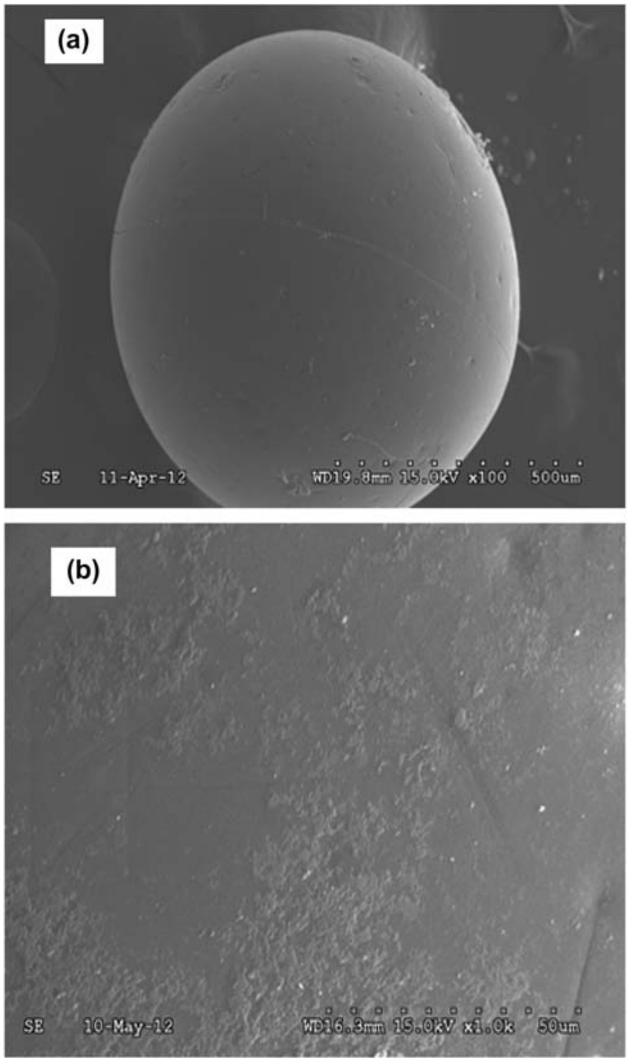

Fig. 5. SEM images of (a) dried unloaded 110 resin and (b) Cu(II)-loaded 110 resin.

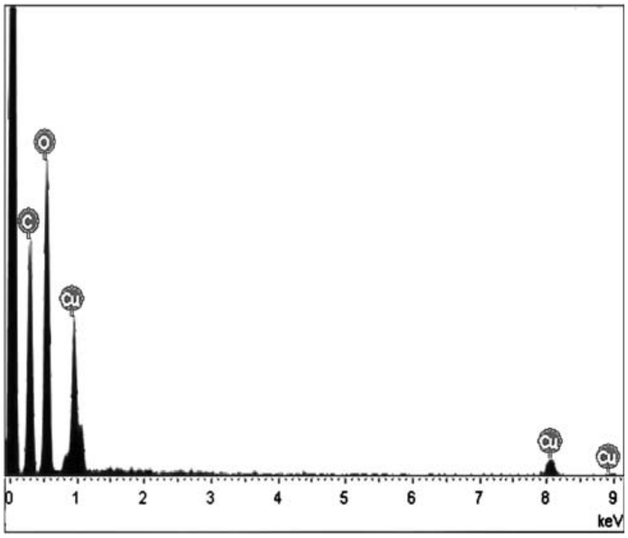

Fig. 6. EDS spectrum of Cu(II)-loaded 110 resin.

In order to confirm the presence of Cu(II) ions in the resin, EDS spectra of the Cu(II)-loaded resin are investigated (Fig. 6). The EDS spectrum of copper-loaded resin showed clearly the peak of copper where intensity is proportional to the metal concentration. Hence, the existence of Cu(II) ion on the 110 resin is confirmed by EDS spectrum. The results revealed that Cu(II) ion were loaded on the surface of 110 resin, which were consistent with the results of SEM.

4. Conclusions

In this study, batch adsorption experiments for the removal of Cu(II) from aqueous solutions had been carried out using 110 resin. The influences of operating parameters such as temperature, initial pH, and initial Cu(II) concentration for the adsorption of Cu(II) on the 110 resin were evaluated using RSM. The RSM analysis demonstrates that optimum adsorption conditions were pH 5.28, 35 ˚C, and initial Cu(II) concentration of 0.34 mg/mL. At optimum adsorption conditions, the adsorption capacity of Cu(II) reached 336 mg/g well in close agreement with the value predicted by the model. It is evident from the experimental data that the adsorption of Cu(II) onto 110 resin obeys the Langmuir isotherm model. Thermodynamic parameters, ΔS, ΔH, and ΔG indicated that the adsorption process was spontaneous and endothermic. The Cu(II) adsorbed on 110 resin can be eluted by using 1.0 mol/L HCl solution as an eluant indicating that the resin can be regenerated and reused. The EDS analysis and IR spectra of Cu(II)-loaded 110 resin were examined to determine the adsorption mechanism of 110 resin. In conclusion, the outcomes from this investigation supported the view that the 110 resin is an effective adsorbent to remove Cu(II) ions from aqueous solutions in the environment protection and wastewater treatment.

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