Optimization of conditions for Cu(II) adsorption on D151 resin from aqueous solutions using response surface methodology and its mechanism study

Hao Zhang, Chunhua Xiong, Fang Liu, Xuming Zheng, Jianxiong Jiang, Qunxiong Zheng and Caiping Yao

ABSTRACT
An experimental study on the removal of Cu(II) from aqueous solutions by D151 resin was carried out in a batch system. The response surface methodology (RSM)-guided optimization indicated that the optimal adsorption conditions are: temperature of 35°C, pH of 5.38, and initial Cu(II) concentration of 0.36 mg/mL, and the predicted adsorption capacity from the model reached 328.3 mg/g. At optimum adsorption conditions, the adsorption capacity of Cu(II) was 321.6 mg/g, which obtained from real experiments what were in close agreement with the predicted value. The adsorption isotherms data fitted the Langmuir model well, and the correlation coefficient has been evaluated. The calculation data of thermodynamic parameters (ΔG, ΔS, and ΔH) confirmed that the adsorption process was endothermic and spontaneous in nature. The desorption study revealed that Cu(II) can be effectively eluted by 1 mol/l HCl solution, and the recovery was 100%. Moreover, the characterization was undertaken by infrared (IR) spectroscopy.

Key words | adsorption mechanism, Cu(II), D151 resin, response surface methodology, thermodynamic, wastewater treatment

INTRODUCTION
In recent years, the contamination of water resources by heavy metals has caused major concern due to the indiscriminate disposal of industrial wastewater. Copper is widely used in many fields, such as the paint and pharmaceutical industries. However, excessive amount of copper entering both the water and the human body will cause serious environmental and public health problems (Aziz et al. 2013; Liu et al. 2013). Consequently, the removal of heavy metals from industrial effluents, and various water resources is very important.

In order to remove heavy metal ions from aqueous solutions, many treatment processes have been used, such as chemical precipitation (Matlock et al. 2002), ion exchange, membrane separation (Kondo & Kamio 2002), electrochemical deposition (Sharma et al. 2005) and extraction chromatography (Minowa & Ebihara 2003). Compared with other methods, adsorption via ion exchange mode has increasingly received more attention in water purification applications due to its unique advantage, including good stability, low cost, high capacity for certain metal ions, and it can be reused many times (Misra et al. 2011).

D151 resin with a functional group (-COOH) is a novel polymeric material and it has not only protons that can be exchanged with cations, but it can also coordinate directly with metal ions. Therefore, it is highly suitable for removing heavy metals from industrial wastewater. The adsorption process involves the variation of physicochemical parameters such as pH, temperature, and initial metal concentration. However, few studies have systematically applied statistical methods to investigate the combination of parameters that provides optimum adsorption conditions. response surface methodology (RSM) is proven to be an effective means 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. Therefore, it is less time consuming and more effective than any conventional method (Ye & Jiang 2011; Wang et al. 2011).

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In this work, series of batch experiments were carried out to study adsorption behavior. RSM was first used to determine the optimization of adsorption conditions of Cu(II) on D151 resin. In addition, the equilibrium adsorption isotherm and thermodynamics parameters were also investigated. The resin was characterized with Fourier transform infrared (FT-IR) spectroscopy. The experimental results may provide important information for the removal of Cu(II) ions from aqueous solutions in environmental protection and wastewater treatments.

MATERIALS AND METHODS

Materials

D151 resin was supplied by Naikai University. The standard stock solutions were prepared by dissolving an appropriate amount of CuSO₄·5H₂O in deionized water. Buffer solutions with pH values of 3.00 ~ 7.00 were prepared from an appropriate dilution of 0.4 mol/L HAc and 0.4 mol/L NaAc. KOH·Na₂B₄O₇ with pH 10.00 buffer solutions was prepared from the NaAc, HAc, Na₂B₄O₇, 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 analytical grade reagents.

Apparatus

The Cu(II) was determined with a Shimadzu UV-2550 ultraviolet-visible spectrophotometer (Shimadzu Corporation, Japan). The D151 resin dosage was measured using a Sartorius BS 224S electronic balance (Sartorius Group, Germany). A Mettler Toledo Delta 320 pH meter (Mettler Toledo, China) was used for pH measurement. The sample was shaken in DSHZ-300A and THZ-C-1 temperature-constant shaking machines (Taicang Experimental Equipment Factory, China). The IR spectra were obtained on a Nicolet 380 FT-IR spectrometer (Xiongdi Instrument Company, China). The water used in the present work was purified using a Mol research analysis-type ultra-pure water machine (Xiongdi Instrument Company, China).

Batch adsorption studies

Batch adsorption experiments were performed in conical flasks containing 30 mL adsorption solution and 15.0 mg D151 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 °C) for 24 h. The upper layer of clear solution was taken for analysis until adsorption equilibrium was reached (Zheng et al. 2014).

Experimental design for RSM study

RSM was used to optimize the adsorption conditions of D151 resin for Cu(II) from aqueous solutions. Factor combinations were obtained by the application of a Box-Behnken design (BBD) using Design-Expert software. In this study, the variables, such as temperature, pH, and initial Cu(II) concentration, are selected process parameters on the adsorption capacity of Cu(II) on D151 resin. The levels and independent variables are shown in Table 1.

Analytical method

A solution containing the 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 with KOH· Na₂B₄O₇ buffer solutions at a pH of 10.00 were added. After the addition of purified water to the 25 mL mark of the colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at a wavelength of 493 nm and compared with the blank test. The adsorption capacity (Q, mg/g), distribution coefficient (D, mL/g) and

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Factors</th>
<th>Coded levels</th>
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<tbody>
<tr>
<td>A</td>
<td>Temperature (°C)</td>
<td>-1 25 35</td>
</tr>
<tr>
<td>B</td>
<td>Initial pH</td>
<td>3 5 7</td>
</tr>
<tr>
<td>C</td>
<td>Initial Cu(II) concentration (mg/mL)</td>
<td>0.20 0.30 0.40</td>
</tr>
</tbody>
</table>
desorption ratio (E, %) (Yu et al. 2012) were calculated with the following formulas:

\[
Q = \frac{C_0 - C_e}{W} V \quad (1)
\]

\[
D = \frac{C_0 - C_e}{W \times C_e} V \quad (2)
\]

\[
E = \frac{C_d V_d}{(C_0 - C_e)} \times 100\% \quad (3)
\]

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of metal ions in solution (mg/mL); \( C_d \) is the concentration of metal ions in desorption solution; \( V \) and \( V_d \) are the total volume of solution and desorption solution (mL); and \( W \) is resin dry weight (g).

**RESULTS AND DISCUSSION**

**Analysis of variance (ANOVA) and development of regression model equation**

BBD was used to develop a correlation between the adsorption conditions and adsorption capacity. A total of 17 runs for optimizing the three individual parameters of the BBD were used to determine the experimental error. As shown in Table 2, the model has good significance with an \( F \)-value of 54.60, and a sufficient probability value \( (< 0.001) \). The determination coefficient \( (R^2 = 0.9860) \) and adjusted \( (R^2_{\text{adj}} = 0.9679) \) demonstrate adequacy of the model under experimental conditions. Moreover, the lack-of-fit value \( (4.85) \) of the model implies non-significance, which is desirable. Adequate precision measures the signal-to-noise ratio and a ratio greater than 4 is desirable. The value of an adequate precision ratio of 21.734 indicates adequate model discrimination (Ghevariya et al. 2011).

From the discussion above, it can be seen that the model has adequate precision. To analyze the adsorption capacity, the following mathematical model, in terms of coded factors, was developed using Design Expert software:

\[
y = 295.68 + 56.59A + 23.79B + 32.65C + 6.17AB - 8.25AC + 21.20BC - 45.13A^2 - 78.95B^2 - 20.65C^2 \quad (4)
\]

The \( p \)-values show the significance of coefficients and are also important for understanding the relationship between the parameters (Ersin et al. 2014). According to the ANOVA (Table 2) A (Temperature), B (Initial pH), C (Initial Cu(II) concentration), \( A^2 \), \( B^2 \), \( C^2 \), BC are the most significant parameters \( (\text{Prob} > F < 0.05) \). However, AB and AC have less effect \( (\text{Prob} > F > 0.05) \) on adsorption capacity.

**The optimization of adsorption conditions**

The results of the adsorption capacity affected by temperature, pH, and initial Cu(II) concentration are shown in panels a, b, and c, respectively, of Figure 1. These types of plots show the effects of two factors on adsorption capacity while the other factor was kept at level zero. From the 3D response surface plots, the optimal values of the parameters could be observed.

The RSM-guided optimization demonstrated that the optimal adsorption conditions for Cu(II) on D151 resin from aqueous solutions are: temperature of 35°C, pH of 5.38, and initial Cu(II) concentration of 0.36 mg/mL, and the predicted adsorption capacity reached 328.3 mg/g. Three batch experiments of the adsorption of D151 resin for Cu(II) were implemented under the predicted optimum conditions in order to validate the mathematical models developed. The mean value of adsorption capacity was 321.6 mg/g, which obtained from real experiments what were in close agreement with the predicted value, indicating...
that the developed model was adequate for predicting the adsorption conditions of D151 resin for Cu(II) from aqueous solutions.

Adsorption isotherm

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between the adsorbate and adsorbent. In this study, the Langmuir and Freundlich isotherms are studied by varying the initial metal ion concentration in the range from 0.20 to 0.40 mg/mL at pH 5.38, 100 rpm and temperatures 288, 298 and 308 K. The Langmuir and Freundlich parameters for the adsorption of Cu(II) are calculated by the following equations.

Langmuir isotherm (Langmuir 1918):

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} 
\]

where \( Q_e \) (mg/g) is the equilibrium of Cu(II) ion concentration on the adsorbent, \( C_e \) (mg/mL) is the equilibrium of Cu(II) ion concentration in solution, \( Q_m \) (mg/g) is the theoretical monolayer adsorption capacity of the adsorbent, \( b \) is the Langmuir constant.

Freundlich isotherm (Freundlich 1906):

\[
\lg Q_e = \lg K_f + \frac{1}{n} \lg C_e 
\]

where \( K_f \) is the Freundlich constant and \( n \) is the heterogeneity factor.

The Langmuir and Freundlich parameters (Xiong et al. 2013) for the adsorption of Cu(II) are listed in Table 3. According to the results, the correlation coefficients' \( R^2 \) values were similar to the initial reports (Wang et al. 2012). We could clearly see from the correlation coefficients that, without doubt, the Langmuir model described the experimental data more precisely than the Freundlich model at the studied temperature. This indicates that the adsorption of Cu(II) by D151 resin is monolayer-type.

Thermodynamic parameters

Adsorption experiments to study the effect of temperature on Cu(II) adsorption by D151 resin were carried out at 288, 298 and 308 K. Thermodynamic parameters, such as standard free energy change (\( \Delta G \)), standard enthalpy change (\( \Delta H \)) and standard entropy change (\( \Delta S \)), were

Table 3 | Isotherm constants for the adsorption of D151 resin for Cu(II) at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tbody>
<tr>
<td></td>
<td>( Q_m ) (mg/g)</td>
<td>( b ) (mL/mg)</td>
</tr>
<tr>
<td>288</td>
<td>297</td>
<td>13.64</td>
</tr>
<tr>
<td>298</td>
<td>341</td>
<td>17.69</td>
</tr>
<tr>
<td>308</td>
<td>372</td>
<td>22.03</td>
</tr>
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</table>
calculated by the following equations (Ünlü & Ersoz 2006):

\[
\lg D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \\
\Delta G = \Delta H - T\Delta S
\]

(7)

(8)

where \( R \) is the gas constant and \( T \) is the absolute temperature. The plot of \( \lg D \) versus \( 1/T \) gives the straight line from which \( \Delta H \) and \( \Delta S \) were calculated. The negative value of \( \Delta G \) (-16.9 to -19.17 kJ/mol) confirms the spontaneous nature of the adsorption and the feasibility of the adsorption process. The positive value of \( \Delta H \) (14.53 kJ/mol) suggests that the adsorption is endothermic in nature. The positive \( \Delta S \) (109.42 J/(K · mol)) value of the Cu(II) adsorption process indicates an irregular increase of randomness at the D151 resin interface during adsorption.

Elution

Whether an adsorbent is economically attractive in the removal of metal ions from aqueous solution depends not only on the adsorptive capacity, but also on how easily and effectively the adsorbent can be desorbed. In this work, different concentrations of HCl were employed in a range from 0.25 to 3.0 mol/L and the following results were obtained. The percentages of elution are 81.35, 90.76, 100, 80.26, and 77.51 for 0.25, 0.5, 1.0, 2.0, and 3.0 mol/L HCl concentration, respectively. It was evident from the data that the maximum percentage of elution for Cu(II) was obtained by using 1.0 mol/L HCl solution as an eluant.

IR spectra

From the above results, it can be deduced that the adsorption process of Cu(II) by D151 resin belongs to chemical adsorption. In order to identify the possibility of Cu(II) bonding to resin, IR spectra were obtained for D151 resin before and after Cu(II) adsorption. It was found that the bands at 3,446 and 3,425 cm\(^{-1}\) are stretching vibrations of the hydroxyl groups, and the bands at 1,718 and 1,560 cm\(^{-1}\) are an indication of C = O. The bands at 1,402 and 1,407 cm\(^{-1}\) are assigned to the peak of band C-OH. It was also found that the characteristic adsorption peak of the band C = O (1,718 cm\(^{-1}\)) weakened after Cu(II) adsorption, and the new peak 1,560 cm\(^{-1}\) was formed. The characteristic peak of the band C-OH shifts from 1,402 to 1,407 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. These results revealed that the C = O groups participate in the adsorption process.

CONCLUSION

In this study, series of adsorption experiments for the removal of Cu(II) from aqueous solution had been carried out using D151 resin. The RSM analysis demonstrates that optimum adsorption conditions were: 35 °C, \( \text{pH} = 5.38 \), and an initial Cu(II) concentration of 0.36 mg/mL. At optimum adsorption conditions, the adsorption capacity of Cu(II) reached 321.6 mg/g, well in close agreement with the value predicted by the model (328.3 mg/g). It is evident from the experimental data that the adsorption of Cu(II) onto D151 resin obeys the Langmuir isotherm model. Thermodynamic parameters, \( \Delta G \), \( \Delta S \), and \( \Delta H \) indicated the adsorption process was endothermic and spontaneous in nature. The Cu(II) adsorbed on D151 resin can be easily eluted by using 1.0 mol/L HCl solution. IR spectra of Cu(II)-loaded D151 resin were examined to determine the adsorption mechanism of D151 resin. In summary, the outcomes for this investigation supported the view that D151 resin has many advantages for removing Cu(II) from aqueous solutions in environmental protection and wastewater treatments.

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