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Study on the treatment of wastewater containing Cu(II) by D851 ion exchange resin

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ABSTRACT

A static adsorption experiment of copper ion was performed with D851 ion exchange resin to determine some optimum treatment parameters. The results of the experiment showed that the enthalpy value of the reaction was positive and the optimum reaction time was 60 min, while the optimum pH value and reaction temperature were 5.5 and 35℃, respectively. The adsorption equilibrium density of 0.1 g ion exchange resin was between 75 and 100 mg/L. With the condition of the hydraulic retention time of 60 min, wastewater containing 10 mg/L Cu(II) (pH ≈ 5.5) was treated by a dynamic ion exchange column, and the treatment effluent can meet the primary standard of the National Integrated Wastewater Discharge Standard (GB8978-1996). Meanwhile a desorption experiment with ion exchange resin was carried out, which determined that the optimum volume fraction of hydrochloric acid solution was 4% in the desorption solution. The figures of the scanning electron microscope showed that the resin saturated with Cu(II) could be regenerated well under the effect of hydrochloric acid solution, which was consistent with the experimental results.

Keywords: Ion exchange resin; Wastewater containing Cu(II); Static adsorption; Dynamic adsorption; Desorption experiment

1. Introduction

Heavy metal pollution has caused wide public concern, as heavy metal ions are non-biodegradable and can be toxic [1,2]. The wastewater from copper smelting industry is complex, which not only pollutes surrounding water environment but endangers human health seriously [3–5]. Furthermore, heavy metal pollution occurs frequently in recent years. The treatment of copper smelting wastewater is not well studied and is being explored to develop new methods of treatment, recovery of valuable metals and industrial waste management [6–9]. Ion exchange resin is used widely in the treatment of the wastewater, especially in heavy metal polluted wastewater [10–13].

Ion exchange resin is a kind of macro molecular compound with mesh structure of functional group, which consisted of three parts: the insoluble polymer with three-dimensional mesh skeleton, multifunctional groups connected with the skeleton and the

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opposite charge exchangeable ions with functional groups. Ion exchange method refers to exchange ions between heavy metal ions and ion exchange resin, which can reduce the concentration of heavy metals in wastewater and can purify wastewater [14,15]. In this study, the static adsorption Cu(II) experiment using D851 ion exchange resin was performed to determine the optimum experimental parameters, which provide important theoretical guidance and technical support for ion resin applied to copper removal engineering.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

All chemicals used in the experiments were of reagent grade or higher and were used as received without further purification: sodium hydroxide (NaOH), copper sulfate ($CuSO_4$), sodium chloride (NaCl), and hydrochloric acid (HCl).

2.1.2. Laboratory apparatus

Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Icap6000 SERIES, Thermo Scientific), constant temperature water bath oscillator, organic glass column (made by ourselves), disposable syringes (10 mL), pipettes, disposable needle filter, and other conventional glass apparatus. All containers and sampling bottles were immersed in 10% HNO_3 solution for 24 h and washed with deionized water.

Synthetic copper solution can be used according to the experiment requirement. The resin employed in this study was D851 resin, obtained from Beijing Zhengguang Industrial Co., Ltd (Beijing, China). D851 is a kind of chelate resin in the special macroporous structure styrene–divinyl benzene copolymer with [–CH_2N–($CH_2OOH)_2$], and some physicochemical indexes were listed in Table 1.

2.2. Methods

Pretreatment: Resin weighed according to the requirement was completely soaked with 5–8% NaCl solution for 6–8 h.

The removal ratio E and adsorbed amount Q were calculated with the following formulas:

$$Q = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

$$E = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}$$

where Q is the adsorption capacity for Cu(II) in equilibrium (mg/g), E is the removal ratio of Cu(II) in equilibrium, C_0 and C_e are, respectively, the initial and equilibrium concentrations of Cu(II), m is the mass of resin (g), and V is the volume of solution (L).

2.2.1. Static adsorption experiment

The static adsorption experiment of copper ions using ion exchange resin is affected by four factors: Reaction time, temperature, pH value, and initial Cu (II) concentration. Equilibrium time experiment has been conducted to find out the sorption equilibrium time of D851 ion exchange resin. Various temperature experiments were carried out to investigate the effect of the sorption velocity and sorption capacity, so that the performance of the resin at different temperature could be obtained. The pH experiments were conducted to investigate the pH effect to the sorption capacity. Resin sorption experiments were conducted with various Cu(II) concentration to find out the effect of initial Cu(II) concentration.

2.2.1.1. Adsorption time study. Resin adsorption equilibrium time and velocity analysis experiment: The initial Cu(II) concentration of test solution is 10 mg/L from copper sulfate solution, which was adjusted to pH ≈ 6 with HCl and NaOH. Hundred milliliter test solution and 100 mg D851 ion

Table 1
Physico-chemical indexes of D851 resin

Item	Framework	Grinding ball rate	Volume exchange capacity (mmol/mL)	Water content (%)	Particle size range	Adsorption capacity (g/L)
Index	Macroporous styrene-divinyl benzene copolymer	≥90.0	≥2.00	55.00–65.00	(0.450–1.250 mm) ≥ 95.0	≥30.0

exchange resin were transferred into conical flasks (250 mL) with cover. The solution was stirred with 200 ± 1 r/min, and the temperature was kept at 25 ± 1 ˚C. Sampled under different reaction time (20, 30, 40, 50, 60, and 120 min), the Cu(II) concentration in the solution was measured by ICP-AES.

2.2.1.2. Reaction temperature effect study. The initial Cu(II) concentration of test solution is 10 mg/L from copper sulfate solution, which was adjusted to pH ≈ 6 with HCl and NaOH. Then, 0.10 g resin was weighed and was transferred into conical flasks (250 mL) with cover, at the same time, 100 mL copper ion solution was transferred to the conical flasks using a pipette. Then, the conical flasks were transferred to a shaker with 200 ± 1 r/min for 60 min, in different reaction temperatures (20, 30, 40, 50, and 60 ˚C).

2.2.1.3. The pH value effect study. The initial Cu(II) concentration of test solution is 10 mg/L from copper sulfate solution, which was adjusted into six different pH values (2, 3, 4, 5, 6, and 7) with HCl and NaOH. Then, 0.10 g × 6 resin were weighed and were transferred into six conical flasks (250 mL) with cover, respectively, at the same time 100 mL × 6 copper ion solution with different initial pH values were transferred to each conical flasks using pipettes. Then, the conical flasks were transferred to the shaker with 200 ± 1 r/min for 60 min.

2.2.1.4. Initial Cu(II) concentration effect study. The test solution was from copper sulfate solution, which were adjusted to six different initial concentration levels (10, 20, 50, 100, 150, 200 mg/L, pH ≈ 6). Then, 0.10 g × 6 resin were weighed and transferred into conical flasks with cover, at the same time, 100 mL copper ion solution ×6 with different initial Cu(II) concentration were transferred to six conical flasks using a pipette, respectively. Then, the conical flasks were transferred to the shaker with 200 ± 1 r/min for 60 min.

2.2.2. Dynamic adsorption and desorption experiments

Dynamic adsorption and desorption experiment was performed in the device (Fig. 1), which contained raw water barrel, constant flow pump, reaction column, pipeline and other two barrels, and so on.

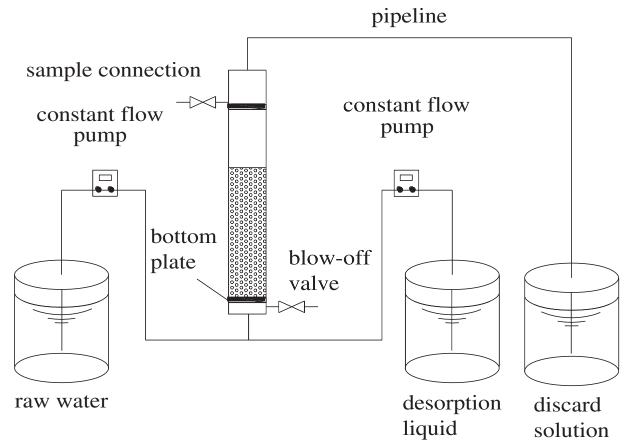

Fig. 1. Dynamic adsorption and desorption experiment device.

The diameter of reaction column was 30 mm and the height was 300 mm, and there was water distribution plate at the bottom of column with 1 mm aperture, which was filled with D851 type ion exchange resin. To examine the dynamic treatment capacity of D851 type ion exchange resin, the wastewater with the initial concentration of 10 mg/L (pH ≈ 5.5, based on the treatment efficiency of static adsorption) was used to conduct the ion sorption experiments. The pretreated resin was soaked in 50 mg/L $CuSO_4$ solution for 2 h, which could make sure that the adsorption of resin was saturated, according to the result of resin adsorption equilibrium time experiment. The resin was used to conduct desorption experiment by sufficient hydrochloric acid solution (volume fraction of the hydrochloric acid was 2, 3, 4, and 5%, respectively).

3. Results and discussion

3.1. Resin adsorption equilibrium time and velocity analysis

It was observed from Fig. 2 that the Cu(II) adsorption quantity of D851 type ion exchange resin rose with the increase in adsorption time on the whole. An abrupt adsorption capacity appeared at the range of 0–60 min and then slowed down until the equilibrium state was reached. The trend could be ascribed to the reaction between metal ions and hydrogen. With the increase in reaction time, the available active sites of the adsorbent reduced gradually until being exhausted, which implies that the concentration of Cu(II) can not decrease any more with the increasing time.

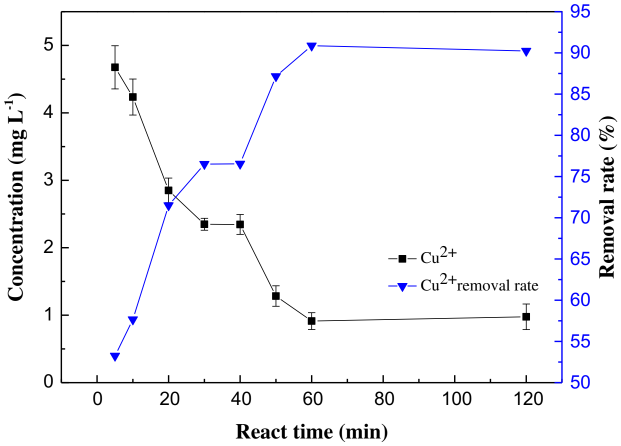

Fig. 2. Relationship of Cu(II) concentration, removal rate, and adsorption time.

3.2. Effects of temperature on ion exchange resin adsorption quantity

The effect of contact temperature on the Cu(II) adsorption process was investigated in the temperature range of 20–60˚C under the adsorption time of 30 and 60 min. As shown in Fig. 3, Cu(II) adsorption capacity increased at the range of 20–40˚C and then slowed down until the equilibrium state was reached. The higher adsorption capacity at higher temperature was due to the greater swelling of the resin and increased the diffusion of metal ions into the resin at higher temperatures [16], which indicated that the adsorption of Cu(II) onto D851 was more effective at higher temperatures. Furthermore, the change in solution temperature also affects the solubility of metal ions [17]. Adsorption process can be affected by temperature in different ways depending on the exothermic or endothermic nature of the process. In this study, as seen in Fig. 3, the adsorption is an endothermic process, which was also proved in 2.5.

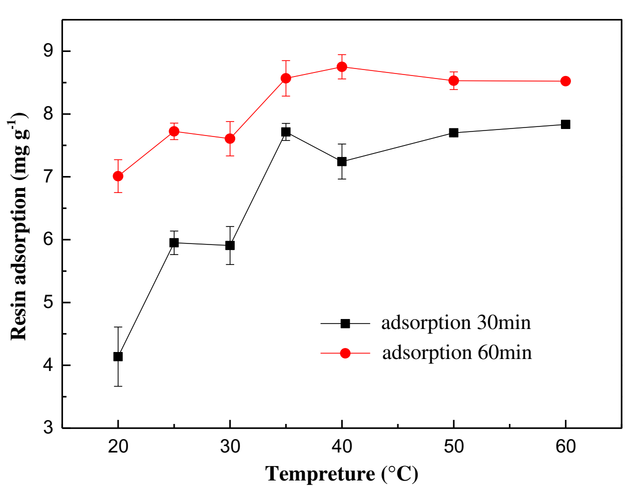

Fig. 3. Effect of temperature on ion exchange resin adsorption quantity.

3.3. Effect of pH on ion exchange resin adsorption quantity

Fig. 4 showed the adsorption of Cu(II) as a function of pH value. When pH value changed from 2.0 to 5.5, an abrupt increase in adsorption capacity was observed and the highest values were achieved around 5.5. The adsorption trends could be ascribed to the competition between metal and hydrogen ions. While at lower pH, both carboxylic groups and nitrogen atom occurred in the protonated form and the active sites of the adsorbent were less available for metal ions due to greater repulsive forces [18]. Meanwhile, the competition between far excess of hydrogen ions and metal existed. In addition, the inhibition of metal chelation with a decrease in pH value had been earlier reported [19,20]. At intermediate pH values, the resin behaved in an amphoteric way, which facilitated the coordination-bond formation [21].

3.4. Relationship of Cu(II) concentration and resin adsorption quantity

With the increase in initial concentration of Cu(II), the resin adsorption quantity increased and then reached equilibrium as shown in Fig. 5. When the initial concentration of Cu(II) was 50 mg/L or less, the adsorption capacity was almost proportional to the concentration of Cu(II), which indicated that ion exchange resin did not reach saturated adsorption

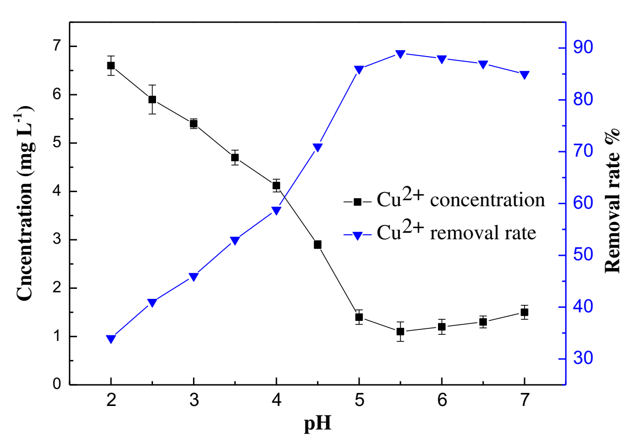

Fig. 4. Effect of pH on ion exchange resin adsorption quantity.

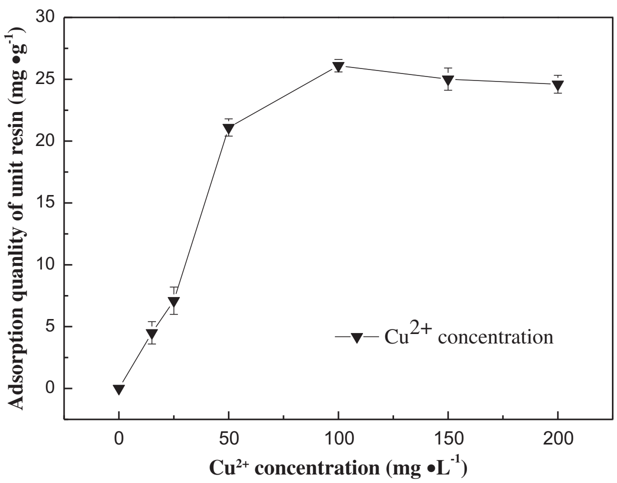

Fig. 5. Relation of Cu(II) concentration and resin adsorption quantity.

amount. When the initial concentration of Cu(II) was around 100 mg/L, adsorption quantity of unit resin reached maximum and the resin reached adsorption saturation state.

3.5. Analysis of adsorption thermodynamic

The experimental data showed in Fig. 4 was described with Langmuir and Freundlich isotherm models, which are shown in (3) and (4), respectively [22,23].

Langmuir adsorption isotherm:

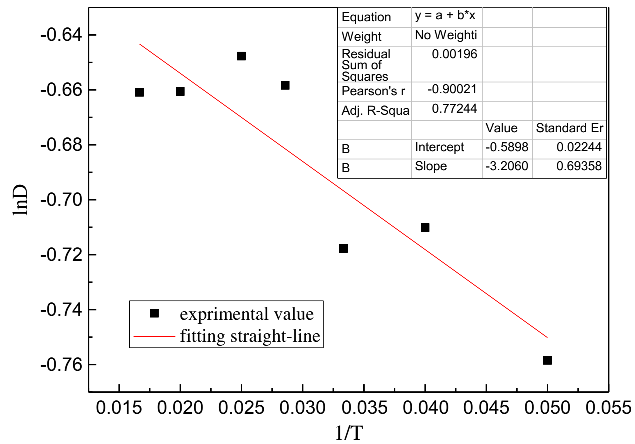

Fig. 7. Typical Van't Hoff plot for adsorption.

$$\frac{c^*}{q^*} = \frac{c^*}{Q_m} + \frac{1}{Q_m K_L} \tag{3}$$

Freundlich adsorption isotherm:

$$\ln q^* = n^{-1} \ln C^* + \ln \mathrm{K_F} \tag{4}$$

where q^* is the equilibrium absorption capacity (mmol/g), C^* is the equilibrium concentration (mmol/L), Q_m is the theoretical maximum adsorption amount, K_L is the Langmuir adsorption equilibrium constant, K_F is the resin adsorption capacity, and n is appetency of resin and adsorbate. The relevant results were showed in Fig. 6.

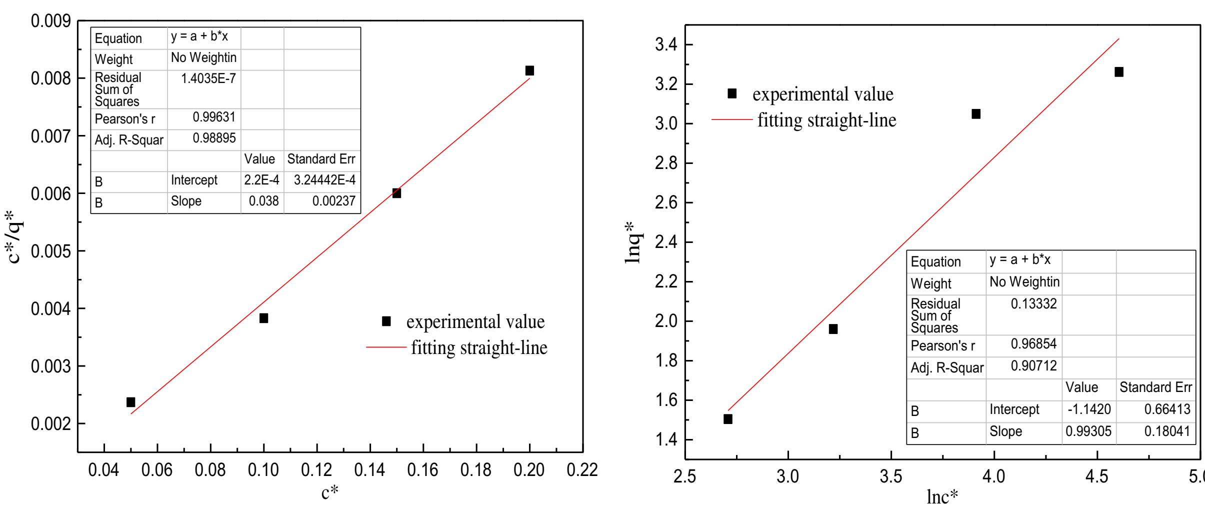

Fig. 6. Fitting plots of the adsorption isotherm with model of Langmuir and Freundlich.

Table 2
Fitting parameters of Langmuir isotherm for the adsorption of Cu(II) on resin

T (K)	Function	Q_m (mmol/g)	K_L (L/mmol)	R^2
308.15	$C_e/Q_e = 0.0389C_e + 0.00022$	25.7069	176.8182	0.9889

Table 3
Thermodynamic parameters for adsorption of Cu(II)

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))
308.15	−13.258	26.6555	12.9527

As shown in Fig. 6, the association coefficient of Langmuir (0.9889) is greater than that of Freundlich (0.9071), which indicates that Langmuir model can preferably describe the adsorption behavior between resin and Cu(II). The parameters are calculated and are tabulated in Table 2.

The thermodynamic parameters provide in-depth information on inherent energetic changes that are associated with adsorption, including the Gibbs free energy ΔG (at equilibrium), the enthalpy change ΔH, and entropy change ΔS (adsorption process), which can be, respectively, estimated by the following equation [19,24,25]:

$$\Delta G = -RT \ln K_L \tag{5}$$

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

where K_L is the equilibrium constant, R is the gas constant [8.314 J/(mol K)], T is the Kelvin temperature, ΔG is the Gibbs free energy (kJ/mol), ΔH is the change in enthalpy (kJ/mol), ΔS is the change in entropy [kJ/(mol K)]. From formula (5) the Gibbs free energy could be obtained, $\Delta G = -RT \ln K_L = -13.258$ kJ/mol.

$$\ln D = -\frac{\Delta H}{RT} + C \tag{8}$$

where the adsorption equilibrium coefficient $D = q^*/c^*$.

The adsorption enthalpy change ΔH can be described, as in formula (8). A scattered diagram of ln D and $1/T$ was made and then fitted a straight line (Fig. 7). From the linear plot between ln D vs. $1/T$, the values of ΔH and ΔS could be obtained as the slope and intercept, respectively.

The fitting line equation is $y = -0.5899 - 3.6021x$, and $\Delta H = 26.6555$ kJ/mol. The enthalpy change $\Delta H > 0$ shows that the adsorption is endothermic process, and high temperature is beneficial for adsorption [26]. The entropy change ΔS can be calculated by formula (6), and the calculated values of thermodynamic parameters are presented in Table 3.

In this reaction system, as the calculated results of ΔG, ΔH, and ΔS showed that the adsorption of Cu(II) on D851 resin is a spontaneous process ($\Delta G > 0$), is an endothermic reaction ($\Delta H > 0$), and is an entropy driven process ($\Delta S > 0$).

3.6. Dynamic treatment experiment of wastewater containing Cu(II) using resin

On the basis of the static experiment to determine the optimum operating parameters, the dynamic ion exchange column experiment was conducted to treat wastewater containing Cu(II) prepared according to the test requirement.

The initial concentration of wastewater was 10 mg/L at pH ≈ 5.5, and the hydraulic retention time was 60 min. The effluent Cu(II) concentration was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES), and pH value was measured by pH meter, which was listed in Table 4.

Table 4 showed that the effluent treated by resin dynamic adsorption process meets the secondary standard of The National Integrated Wastewater Discharge Standard (GB8978-1996). With the action of ion exchange resin the removal rate of Cu(II) was high,

Table 4
Result of resin dynamic adsorption experiment

Index	pH	Concentration of Cu(II) (mg/L)
Inflow	5.5	10
Effluent	6.7	0.5
Discharge standard	6–9	0.36

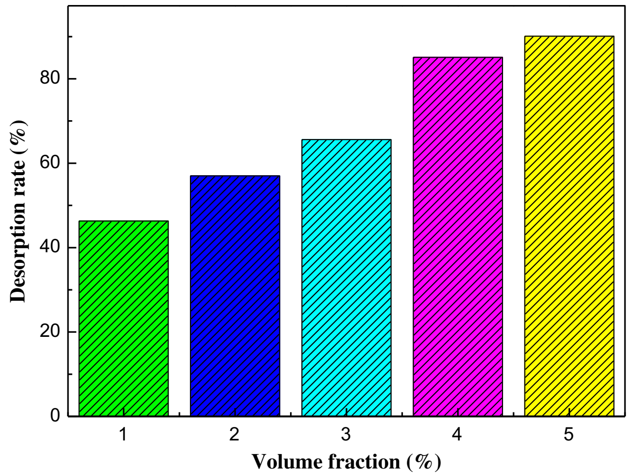

Fig. 8. Effect of hydrochloric acid volume fraction on desorption rate.

which indicated that the ion exchange resin treatment was suitable for secondary treatment or advanced treatment.

3.7. Desorption experiment of ion exchange resin

The pretreated resin was soaked in copper sulphate solution for 2 h, and the hydrochloric acid volume fraction of the solution were 2, 3, 4, and 5%, respectively. The desorption rate was calculated with the following formula:

$$R = \frac{C_2}{50 - C_1} \times 100\% \tag{9}$$

where R is the desorption rate of resin, C_1 is the concentration of Cu(II) in copper sulphate solution, C_2 is the concentration of Cu(II) in hydrochloric acid desorption solution. The desorption rate with the

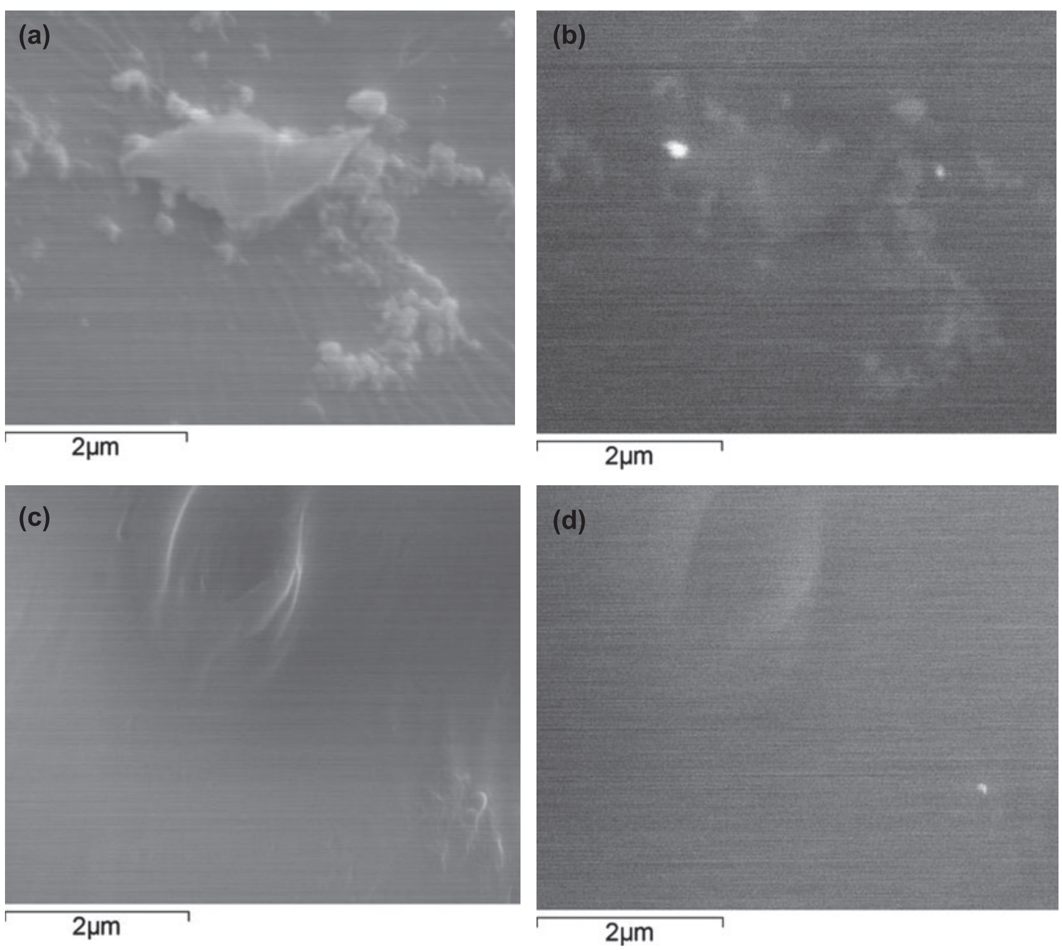

Fig. 9. SEM and back scattering images of resin: (a) SEM image of adsorbed resin; (b) Back scattering image of adsorbed resin; (c) SEM image of desorbed resin; and (d) Back scattering image of desorbed resin.

action of hydrochloric acid desorption solution was shown in Fig. 6.

Fig. 8 showed that the desorption rate of resin rose with the increasing volume fraction of hydrochloric acid. The desorption rate was similar when hydrochloric acid volume fraction was at either 4 or 5%, so the optimum volume fraction was 4%.

Fig. 9(a) showed that a lot of congeries appeared at the surface of resin after the adsorption experiments. Fig. 9(b) back scattering images showed that the congeries were heavy metals, which were consistent with the actual result. Fig. 9(c) showed that the congeries disappeared after desorption experiment. Fig. 9(d) back scattering images showed that heavy metals disappeared obviously, which showed that desorption effect was good for regeneration and was consistent with the actual experimental effect.

4. Conclusion

(1) The optimum experimental conditions of D851 ion exchange resin treating Cu(II) wastewater was obtained by static adsorption experiment: Enthalpy value of the reaction is positive, the optimum reaction time was 60 min, the optimum reaction temperature was 35℃ while the optimum pH value was 5.5.

(2) Wastewater containing 10 mg/L Cu(II) was treated by ion exchange resin dynamic adsorption, and the effluent quality can meet the primary standard of The National Integrated Wastewater Discharge Standard (GB8978-1996).

(3) The desorption of ion exchange resin result showed that the desorption rate of saturated adsorption resin rose with the increase in the hydrochloric acid volume fraction. However, the difference between 4 and 5% of the hydrochloric acid volume fraction almost disappeared, so the advised volume fraction of the hydrochloric acid was 4%.

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