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Adsorption of copper using macroporous phosphonic acid resin ①

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Abstract: The adsorption behavior and mechanism of a novel chelate resin, macroporous phosphonic acid resin(PAR) for Cu(Ⅱ) were investigated. The statically saturated Cu(Ⅱ) adsorption capacity is 168 mg/g resin at 298K in HAc-NaAc medium. The Cu(Ⅱ) adsorbed on PAR can be eluted by 1.0－3.0 mol/L HCl and the elution percentage reaches 100%. The resin can be regenerated and reused without apparent decrease in adsorption capacity. The apparent adsorption rate constant is $k = 1.64\times10^{-4}\ s^{-1}$ at 298K. The adsorption behavior of PAR for Cu(Ⅱ) obeys the Freundlich isotherm. The thermodynamic adsorption parameters, enthalpy change ΔH, free energy change ΔG and entropy change ΔS of PAR for Cu(Ⅱ) are 11.8 kJ/mol, －2.0 kJ/mol and 46.4 $J\cdot mol^{-1}\cdot K^{-1}$ respectively. The apparent activation energy is $E_a = 8.0$ kJ/mol. The molar coordination ratio of the functional group of PAR to Cu(Ⅱ) is about 2:1. The adsorption mechanism of PAR for Cu(Ⅱ) was examined by chemical method and IR spectrometry.

Key words: macroporous phosphonic acid resin; copper; adsorption; mechanism
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1 INTRODUCTION

The research papers about synthesis characterization and adsorption property of polymeric materials have been published in recent years[1-5]. Macroporous phosphonic acid resin (PAR) is a novel polymeric material which contains a functional group of [－PO(OH)$_2$]. It has quite a lot of advantages such as high adsorption capacity, easy regeneration and convenient operation. So PAR can be used well in the adsorption of metal ions. But so far, there hasn't been a report on adsorption for Cu(Ⅱ) which is one of important elements in hydrometallurgy[6-9]. In this paper, we describe the adsorption behavior and mechanism of PAR for Cu(Ⅱ). The basic adsorption parameters were determined. The experimental results may be applied to concentrate copper in hydrometallurgy and analytical chemistry and may also be used in the treatment of waste water containing copper element.

2 EXPERIMENTAL

2.1 Materials

Macroporous PAR was provided by Nankai University(H-type, activated before use), standard solution of Cu(Ⅱ) was prepared from CuO(AR), buffer solution with pH 2.0－6.0 were prepared from KCl-HCl and HAc-NaAc, and other reagents were AR grade.

2.2 Instruments

722 spectrophotometer, sartorius PB-20 pH meter, SHZ-B temperature constant shaking machine, Perkin-Elmer 683 FT-IR, and elemental analyzer EA 1110 were used.

2.3 Method

2.3.1 Adsorption equilibrium experiment

A desired amount of treated resin was weighted and added into a conical flask, then a desired volume buffer solution of pH 5.6 was added. After 24 h, a required amount of standard solution of Cu(Ⅱ) was added. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium was reached. The adsorption amount(Q) and distribution coefficient(D) was calculated with the formula:

$$D = \frac{(c_0 - c_e)}{c_e}\cdot\frac{V}{w} = \frac{Q}{c_e} \quad (1)$$

where c_0 is initial concentration of metal ion in solution (mg/mL), c_e is equilibrium concentration of metal ion in solution(mg/mL), V is total volume of solution(mL), and w is resin mass(g).

2.3.2 Analytical method

Solution containing Cu^{2+} lower than 36 μg was

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accurately added into a 25 mL colorimetric tube, and then 1.0 mL 0.5% xylenol orange solution and 10.0 mL $(CH_2)_6N_4$-HCl buffer solution with pH of 5.7 were added. After the addition of redistill water to the mark of colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 555 nm and compared with blank test.

2.3.3 Elution test

20.0 mg resin was added into a mixed solution composed with buffer solution (pH = 5.6) and desired amount of standard solution of Cu(II). After equilibrium reached, the concentration of Cu(II) in the aqueous phase was determined, and then the adsorption capacity of the resin for Cu(II) was obtained.

The resin separated from aqueous phase was washed three times with buffer solution with pH of 5.6. The resin adsorbed Cu(II) was shaken with eluant. After equilibrium reached, the concentration of Cu(II) in aqueous phase was determined and then the percentage of elution was obtained.

3 RESULTS AND DISCUSSION

3.1 Effect of pH on distribution coefficient

The test was carried out according to the method mentioned above. The effect of pH on the adsorption behavior of PAR for Cu^{2+} is shown in Fig. 1. The results indicate that the distribution coefficient increase with the increase of pH and almost keep steady when pH is above 5.0. In order to prevent Cu^{2+} from hydrolyzing, all the following experiments were performed at pH = 5.6.

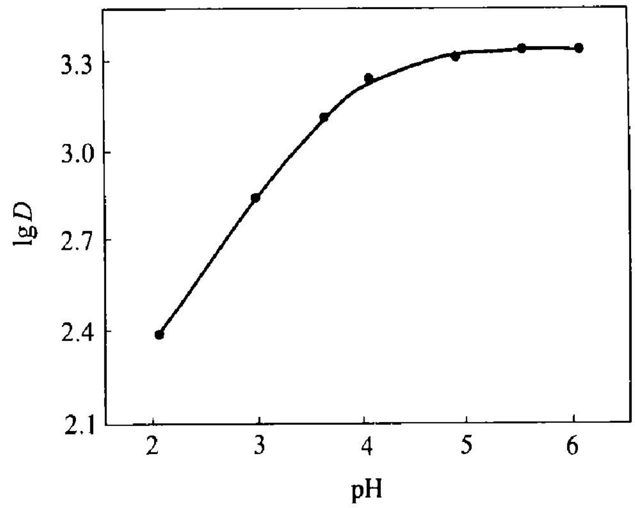


Fig. 1 Effect of pH on distribution coefficient
(w_{resin} = 20.0 mg, T = 298K, $c_0(Cu^{2+})$ = 2/15 mg/mL)

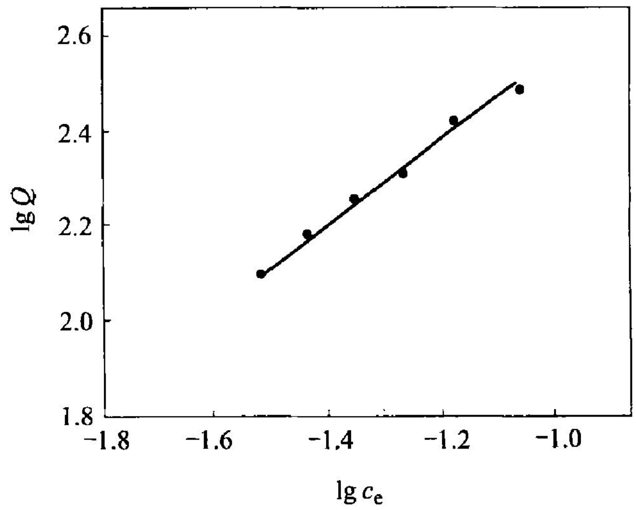


Fig. 2 Freundlich isotherm curve
(T = 298 K, pH = 5.6, $c_0(Cu^{2+})$ = 1/5 mg/mL)

3.2 Isotherm adsorption curve

20.0 mg, 25.0 mg, 30.0 mg, 35.0 mg, 40.0 mg and 45.0 mg resin were put into conical flasks individually. The experimental conditions are shown in Fig. 2. When the adsorption equilibrium was reached, equilibrium concentration (c_e) was determined and corresponding adsorption capacity Q (mg/g resin) was calculated and plotted in Fig. 2. The adsorption isotherm is further correlated to the well-known Freundlich equation:

$$Q = a c_e^{1/b}$$

$$\lg Q = 1/b(\lg c_e) + \lg a$$

where b and a are characteristic constants. The regression equation at 298 K is

$$\lg Q = 0.416\,5 \lg c_e + 2.691\,7$$

The correlation coefficient is 0.998 7. So, b is 2.4 and a is 491.7. The fact that b is between 2 and 10 indicates that Cu(II) is easily adsorbed[10].

3.3 Determination of adsorption rate constant and apparent activation energy

According to the experimental conditions shown as Fig. 3 and the above-mentioned method, 0.15 mL upper layer clear solution was taken out at intervals for the determination of remained concentrations. After the remains kept constant and volume was corrected, a series of data were obtained. When the adsorption amount is half of that at equilibrium, the required time $t_{1/2}$ is 1 h. According to Brykina method[11],

$$-\ln(1-F) = kt \qquad (2)$$

where $F = Q_t/Q_\infty$, Q_t and Q_∞ are the adsorption amounts at certain time and equilibrium respectively. The experimental results are accorded with the Eqn. (2) and a straight line is obtained by plotting $-\ln(1-F)$ vs t. Therefore, the adsorption rate constant k at 298K can be found out from the slope of the straight line, $k = 1.64 \times 10^{-4}\ s^{-1}$. It can be known from the linear relationship between $-\ln(1-F)$ and t that the liquid film spreading is the predominant step of the adsorption process. At different temperatures (290 K, 308 K and 318 K), the adsorption rate constants were measured too. Plotting of lg$k$ vs $1/T$ shown as Fig. 4, a straight line is got, whose slope is $k' = -0.4189 \times 10^3$ and the correlation coefficient is 0.9976. According to Arrhenius equation:

$$\lg k = -E_a/2.303RT + c \qquad (3)$$

the apparent activation energy E_a is 8.0 kJ/mol, c is constant.

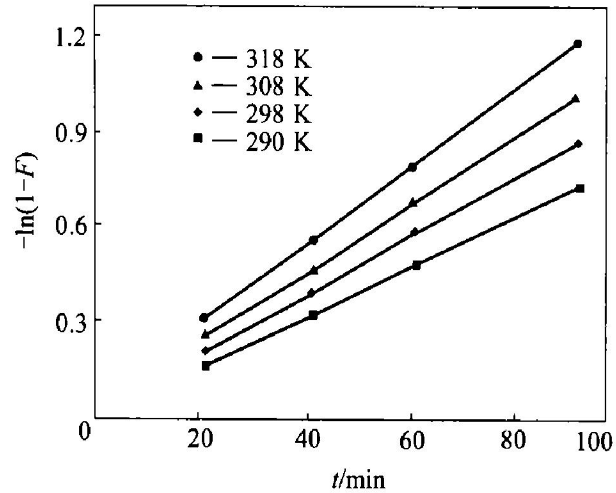


Fig. 3 Determination of adsorption rate
(w_{resin} = 20.0 mg, pH = 5.6, $c_0(Cu^{2+})$ = 3/25 mg/mL)

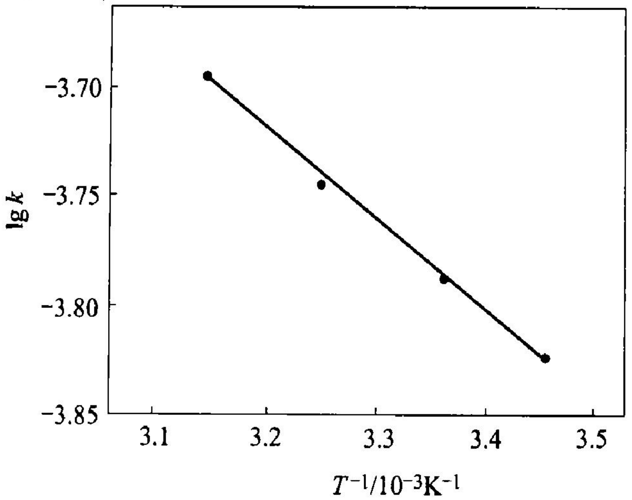
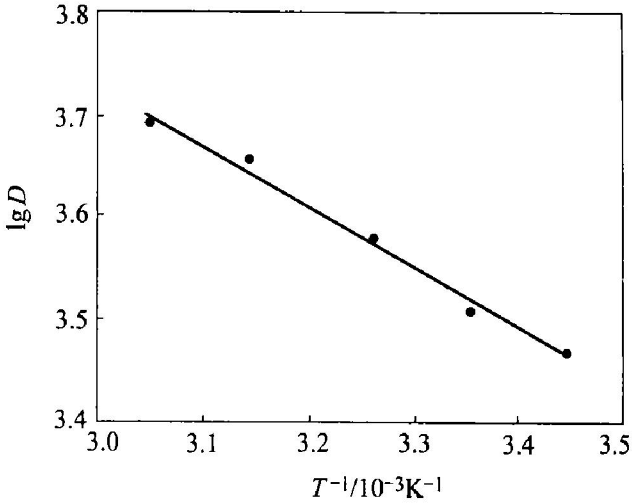


Fig. 4 Plotting of lg$k$ vs $1/T$
(w_{resin} = 20.0 mg, pH = 5.6, $c_0(Cu^{2+})$ = 3/25 mg/mL)

3.4 Effect of adsorption temperature on distribution coefficient and determination of thermodynamic parameters

Under the experimental condition shown in Fig. 5, distribution coefficient of the resin for Cu^{2+} during the range of temperature from 290 K to 318 K was measured. A straight line was obtained by plotting lg$D$ vs $1/T$ with a correlation coefficient of 0.9978. The result indicates obviously that distribution coefficient increases with increasing of the adsorption temperature. It indicates that the adsorption process is an endothermic process. So, the adsorption reaction is a chemical adsorption. According to the following equation:



g. 5 Effect of temperature on distribution coefficient
(w_{resin} = 20.0 mg, pH = 5.6, $c_0(Cu^{2+})$ = 1/6 mg/mL)

$$\lg D = -\Delta H/2.303RT + \Delta S/R \qquad (4)$$

ΔH can be found out, which is 11.8 kJ/mol; ΔS can be obtained from the intercept of the line, which is 46.4 J/(mol·K).

The adsorption reaction is a spontaneous reaction under the experimental condition of T = 298 K, and the result ΔG is −2.0 kJ/mol.

3.5 Determination of complex ratio

3.5.1 Saturated capacity method

Under the experimental condition of T = 298 K, $c_0(Cu^{2+})$ = 1/6 mg/mL, the experiment was performed by using the above-mentioned method. The adsorption capacity of the resin for Cu^{2+} was 168 mg/g resin. The amount of functional group and the capacity of the resin for Cu^{2+} were calculated as Table 1, which indicates that the molar ratio of the functional group to Cu(Ⅱ) is 2∶1 approximately.

Table 1 Complex molar ratio of PAR functional group to Cu(Ⅱ)

P content of PAR/%	Functional group capacity of PAR/(mmol·g^{-1})	Adsorption capacity of PAR/(mmol·g^{-1})	Complex ratio
15.75	5.08	2.65	1.92∶1

3.5.2 Equimolar method

Seven parts of different amounts of resins were accurately weighted and added into the conical flasks, then mixed with different amounts of Cu(Ⅱ). The total PAR and Cu(Ⅱ) was kept at 145.0 μmol whatever the molar ratio might be. The experiment was carried out with the same method mentioned. The curve of adsorption amount vs [R]/([Cu^{2+}] + [R]) is shown in Fig. 6. The expected adsorption amount is the biggest where the molar fraction of Cu(Ⅱ) is 0.33. It means that the complex ratio of the functional

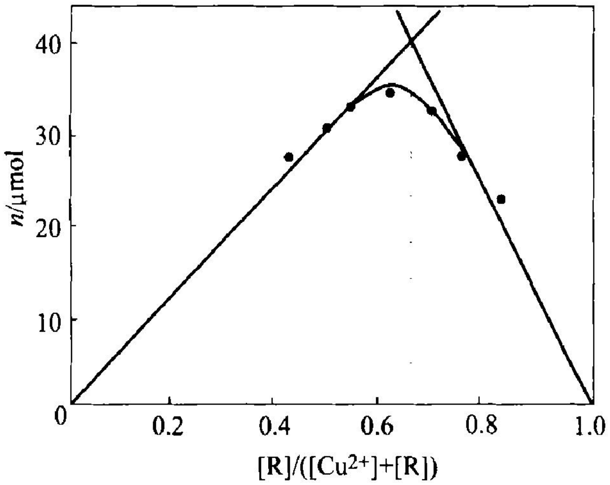


Fig. 6 Curve of adsorption amount n vs $[R]/[Cu^{2+}]+[R]$
(T = 298 K, pH = 5.6, n_{total} = 145.0 μmol)

group to Cu is about 2∶1.

3.6 Analysis of infrared spectra

The above result shows that the adsorption of Cu(Ⅱ) by PAR($\Delta H > 0$) belongs to chemical adsorption. Therefore, in the functional groups of PAR, P ═ O, P — OH and Cu(Ⅱ) are supposed to form chemical bonds. In order to confirm this, we compared the spectra of the resin before and after Cu(Ⅱ) adsorbed, as shown in Fig. 7. It is easy to discover that the characteristic adsorption peaks of the bond P ═ O shifts from 1 160 cm^{-1} to 1 125 cm^{-1} and from 905 cm^{-1} to 925 cm^{-1}, which shows that the formation of the coordination of the oxygen and Cu(Ⅱ) weakens the stretch contraction vibration and causes the peak to shift to the lower frequency. The peak shifted from 1 660 cm^{-1} to 1 625 cm^{-1} indicates that H of P — OH has been replaced. All those results in the formation of complex compound.

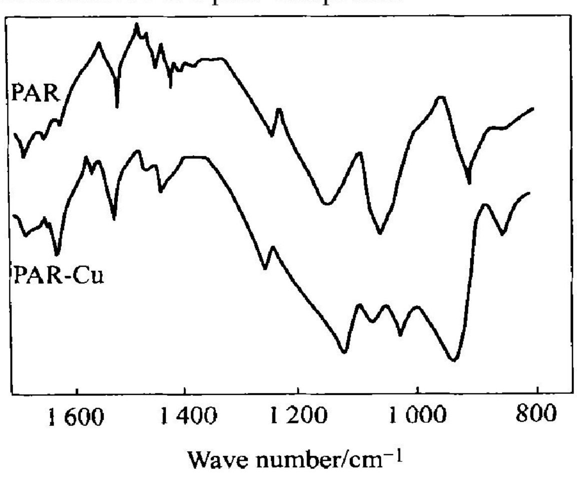


Fig. 7 IR spectra of the resin before and after Cu(Ⅱ) adsor

3.7 Elution and recovery of resin

When HCl was used as an eluant, the percentage of elution are listed in Table 2. Experimental results show that the percentages of elution reach 100% when the concentration of HCl varies from 1.0 mol/L to 3.0 mol/L. So Cu(Ⅱ) adsorbed on the resin can be recovered quantitatively.

In order to examine the practical value of HCl as an eluant, the elution rate of 1.0 mol/L HCl was determined by using the same method mentioned above. The results show that $t_{1/2}$ is equal to 1 min, which is the time required to reach 50% of elution. Therefore, the elution of Cu(Ⅱ) is practical from the point view of kinetics.

Table 2 Elution test of Cu(Ⅱ)

Concentration of HCl/ (mol·L^{-1})	Elution percentage/ %
0.5	95.8
1.0	100.0
2.0	100.0
3.0	100.0

3.8 Regeneration and reuse of PAR

After Cu(Ⅱ) was adsorbed and eluted by 1.0 mol/L HCl, the resin was washed several times by redistilled water. Three regeneration test were carried out. The results listed in Table 3 show that adsorption capacity is almost not changeable and that PAR can be regenerated. The resin can be regenerated and reused.

Table 3 Results of reuse of PAR

Reuse times	Adsorption capacity/ (mg·g^{-1})
1	168
2	167
3	167

The IR spectrum of the regenerated resin is exactly the same as that of PAR and P content of the regenerated PAR equals to that of the original PAR too. The results show that the quality of regenerated PAR is good.

4 CONCLUSIONS

1) Results of the adsorption experiment show that Cu(Ⅱ) can be optimally adsorbed on macroporous phosphonic acid resin in the HAc-NaAc system at pH = 5.6. The statically saturated adsorption capacity is 168 mg/g resin at 298 K. The Cu(Ⅱ) adsorbed on PAR can be eluted by using 1.0 − 3.0 mol/L HCl quantitatively. The resin can be regenerated and reused without apparent decrease

of adsorption capacity.

2) The apparent adsorption rate constant is $k = 1.64 \times 10^{-4}\ s^{-1}$ at 298K. The adsorption behavior of PAR for Cu(Ⅱ) obeys the Freundlich isotherm. The thermodynamic adsorption parameters are $\Delta H = 11.8$ kJ/mol, $\Delta G = -2.0$ kJ/mol, $\Delta S = 46.4$ J/(mol·K) respectively. The apparent activation energy was measured to be 8.0 kJ/mol.

3) PAR can concentrate, separate and recover Cu(Ⅱ) in the HAc-NaAc system. The adsorption capacity of PAR for Cu(Ⅱ) is high, and the operation is simple and convenient.

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