Adsorption and Desorption of Copper(II) from Solutions on New Spherical Cellulose Adsorbent

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ABSTRACT: An investigation was conducted on the adsorption and desorption of copper(II) from aqueous solutions with a new spherical cellulose adsorbent containing the carboxyl anionic group. Various factors affecting the adsorption were optimized. The adsorption of Cu^{2+} ions on the adsorbent was found to be dependent on the initial time and pH, the concentration, and the temperature. The adsorption process follows both Freundlich and Langmuir adsorption isotherms and was found to be endothermic (ΔH = 23.99 kJ/mol). The Cu^{2+} ions adsorbed on the adsorbent can be recovered with a NaOH or HCl aqueous solution. The maximum percentage of recovery is about 100% when 2.4 mol/L HCl solution is used. In addition, only 7.2% of the adsorption capacity is lost after 30 replications of the adsorption and desorption. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 478–485, 2002; DOI 10.1002/app.10114

Key words: spherical cellulose adsorbent; graft; copper(II); adsorption; desorption

INTRODUCTION

Copper and its compounds are ubiquitous in the environment and thus are frequently found in bodies of water. The copper ion (Cu^{2+}) can significantly affect the ecological environment when present in large amounts. Excessive human intake of large doses of copper can lead to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression.[1,2] Moreover, severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also occur due to chronic copper poisoning.[1] Copper(II) is also toxic to fish life, even when its content is small in natural waters.[1] Therefore, the concentration of Cu^{2+} in water is controlled within a allowable limit in each country. In China the allowable limits of copper(II) in drinking water and irrigation water are 0.5 and 1.0 mg/L, respectively.[3,4] In the meanwhile, the increasingly stringent discharge limits force such industries as metal finishing, paper and pulp, fertilizers, and so forth to take effective measures to control copper pollution.

The methods for copper(II) removal from wastewaters include precipitation, ion exchange, electrolysis, adsorption, membrane separation, and so forth.[5,6] As one of the above common methods to remove toxic substances from wastewaters, adsorption at the solid–solution interface is an

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important means for controlling the extent of pollution due to metallic species of industrial effluents.[7,8] Furthermore, numerous investigations have proved the feasibility of use of agricultural products and by-products, industrial waste biomass, and natural substances to adsorb and accumulate heavy metals.[9–15] These materials are also readily available and inexpensive. Therefore, the adsorption phenomenon is still economically appealing for the removal of toxic metals from wastewaters by choosing some adsorbents under optimum operation conditions.

Cellulose is one of the most abundant renewable natural polymers on earth. In addition, it has three reactive hydroxyl groups in each constituent anhydroglucose unit. Consequently, cellulose is a very promising raw material for the preparation of various functional polymers. Many investigators have done work on the modification of cellulose.[11,14–17] Modified celluloses have been successfully used to adsorb metal ions.[13–15] In the case of cellulose adsorbents, the powder, fine particle, and fibriform shapes are dominant current shapes. In order to improve the surface area, permeability, and hydraulic performance of the cellulose adsorbent, a new kind of adsorbent, which is a spherical cellulose adsorbent of metal ions (SCAM-1), was developed in this work to meet the needs of bed adsorption and thus to further increase adsorption efficiency.[18] This article reports on the preparation of SCAM-1 and the effects of time, concentration, pH, salt, and temperature on the adsorption of Cu^{2+} ions in solutions. The Langmuir constant and thermodynamic parameters of adsorption in a temperature range of 10–40°C, as well as Freundlich parameters, were also investigated. Recovery and regeneration tests and comparison tests were conducted to assess the practical utility of the adsorbent.

EXPERIMENTAL

Materials

Cotton was used as the cellulose material. Transformer oil was used as industrial grade. In addition to cupric sulfate (analytical grade), we used acrylonitrile, carbon disulfide, sodium hydroxide, sodium chloride, nitric acid, sulfuric acid, and hydrochloric acid (all reagent grade, Chengdu Chemical Co., Sichuan, China). A weakly acidic cation exchange resin, 724 (R724) was provided by Chengdu Chemical Co.

Instruments

A low-pressure ion chromatograph (model ZJ-4, Modern Separation & Analysis Laboratory, College of Light Industry and Food Engineering, Sichuan University, Chengdu, China) equipped with an electronic peristaltic pump (model LDB-09, Xianshan Instrument and Meter Plant, Zhejing, China) and an optical flow cell (made by X.Z.) was used to determine the content of Cu^{2+} ions. A water-bath oscillator (model HZS-H, Haerbin Dongliang Electronic Technique Exploitation Co. Ltd., Haerbin, China) was applied in the adsorption and desorption experiments. A pH meter (model PHS-3C, Shanghai Second Analytical Instrument Factory, Shanghai, China) was adopted to measure the acidity of the copper(II) solutions.

Synthesis of SCAM-1 Adsorbent

Cotton viscose was made by basification, aging, xanthation, and dissolution of the raw cotton material. After adding a calculated amount of surfactants into the viscose, the mixture was evenly mixed with the transformer oil to prepare spherical cellulose beads with a particle diameter of 0.8–1.2 mm by applying the thermal solution–gel transition technique.[18]

Sixty grams of spherical cellulose beads with 75.3% moisture content were slurried in 90 mL of water. After stirring for 10 min at ambient temperature, 30 mL of a 1.2% mixed initiator aqueous solution was added. Then a calculated amount of acrylonitrile (acrylonitrile/cellulose = 2.4:1, mol/mol) was added to the above solution over 5 min. After 1.0 h a 10% NaOH aqueous solution was added, and the mixture was stirred for 2.0 h while the temperature of the solution was raised and maintained at 75°C. Then the mixture was cooled and filtered, and the pH was adjusted to 6.5 with a 0.6 mol/L HCl aqueous solution. After filtering, washing, and drying, the spherical cellulose adsorbent containing the carboxyl anionic groups was obtained. This adsorbent was denoted as SCAM-1. Some properties of SCAM-1 are given in Table I.

Adsorption Experiments

Batch adsorption experiments were carried out by shaking 0.4 g of SCAM-1 adsorbent (50.1% H_2O) with 100 mL of an aqueous solution of Cu^{2+} ions of the desired concentration, pH, and temperature in different glass-stoppered Erlenmeyer flasks at a constant speed of 80 rpm for predeter-

Table I   Properties of SCAM-1

Particle diameter (mm)	0.8–1.2	Mean pore diameter (nm)	20.71
Surface area (m²/g)	189.12	Porosity (%)	50.53
Specific density (g/mL)	1.043	Moisture content (%)	50.1
Apparent density (g/mL)	0.516	Capacity (mmol/g)	3.66
Pore volume (mL/g)	0.979		

mined time intervals. The concentration of Cu^{2+} ions was analyzed by low-pressure ion chromatography.[19,20] The concentration of Cu^{2+} ions adsorbed was calculated by the difference of the concentration of Cu^{2+} ions in solution before and after adsorption.

Desorption and Readsoption Experiments

Recovery of adsorbate and regeneration of adsorbent is a key process in the wastewater process. In order to achieve these two purposes and to assess the practical utility of the adsorbent, desorption experiments were conducted by treating 0.4 g of SCAM-1 with adsorbed Cu^{2+} ions with 10 mL of the desired concentration of HCl or NaOH aqueous solution for a predetermined time. The readsorption experiments were conducted by using the SCAM-1 desorbed according to the procedures of the adsorption experiments. The concentration of Cu^{2+} ions was analyzed by the difference of the concentration of Cu^{2+} ions in the solution before and after desorption.

RESULTS AND DISCUSSION

Establishing of Linear Equation of Cu^{2+} Ions

The concentration of Cu^{2+} ions was determined by low-pressure ion chromatography. The following equation was obtained by linear regression analysis of the determination results.

$$y = 1.1670x - 16.06 \quad \gamma = 0.9982 \qquad (1)$$

where x is the concentration of Cu^{2+} ions (mg/L), y is the peak height (mm), and γ is the correlation coefficient indicating the linear relationship between x and y.
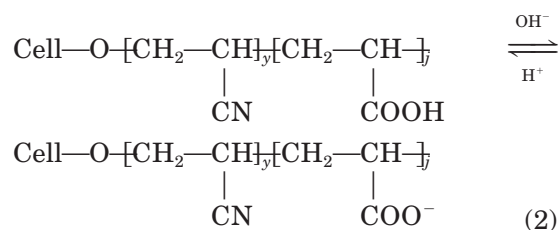
Effect of Adsorption Time

Figure 1 illustrates the effect of the adsorption time on the adsorption efficiency. The removal rate of Cu^{2+} ions increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 120 min, which indicates that the adsorption tends toward saturation at 120 min. Therefore, the adsorption time was set to 120 min in each experiment.

Effect of Solution pH

The effect of the solution pH on the adsorption of Cu^{2+} ions on SCAM-1 is presented in Figure 2. The solution pH is an important controlling parameter in the adsorption process, and thus the role of hydrogen ion concentration was examined from solutions at pH 2.0–6.0. Figure 2 shows that with an increase in the pH of the solution of Cu^{2+} ions, the removal percentage increases from 24.1 to 99.8%.

The hydrolysis of SCAM-1 in the aqueous solution can be expressed as

$$\text{Cell—O—[CH}_2\text{—CH]}_y\text{[CH}_2\text{—CH—]}_j \underset{H^+}{\overset{OH^-}{\rightleftharpoons}}$$
$$\qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad CN \qquad\quad COOH$$

$$\text{Cell—O—[CH}_2\text{—CH]}_y\text{[CH}_2\text{—CH—]}_j$$
$$\qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad CN \qquad\quad COO^- \qquad (2)$$

The hydrolysis of Cu^{2+} ions also occurs simultaneously in the aqueous solution, and the degree of
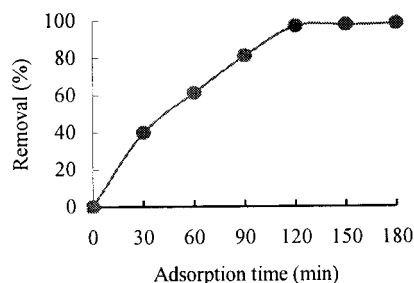

Figure 1   The effect of the adsorption time on the adsorption of Cu^{2+} ions on SCAM-1 at pH 5.0 and 10°C with 63.5 mg/L Cu^{2+}.
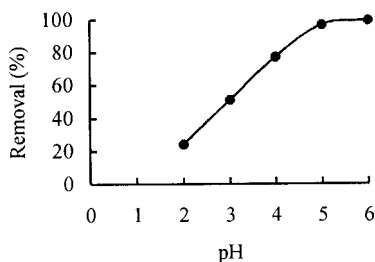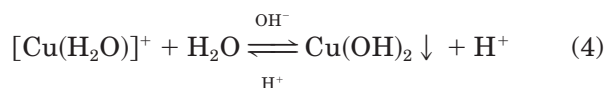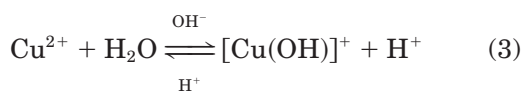
Figure 2 The effect of the solution pH on the adsorption of Cu^{2+} ions on SCAM-1 at 10°C for 120 min with 63.5 mg/L Cu^{2+}.

hydrolysis increases with the increase in the pH of the solution. The reaction may be written as

$$Cu^{2+} + H_2O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Cu(OH)]^+ + H^+ \qquad (3)$$

$$[Cu(H_2O)]^+ + H_2O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Cu(OH)_2 \downarrow + H^+ \qquad (4)$$

Therefore, it can be inferred that the solution pH not only affects the surface charge of the adsorbent (SCAM-1), but also inferences the degree of ionization and speciation of the adsorbent (Cu^{2+} ions). This inference agrees with the conclusion suggested by Elliott and Huang.[7] Stumm and Bilinski also proposed that the adsorption of metal ions at the solid–solution interface is not governed by the "free" metal concentration but is instead governed by the much stronger adsorbed hydroxo, sulfato, carbonato, and other metal species.[21] Hence, the increase in the pH of the solution can promote the chelation of carboxyl groups in SCAM-1 with Cu^{2+} ions to form the chelates in the adsorption process.

Baes and Mesmer reported that as the solution pH increased, the onset of metal hydrolysis and precipitation (at a metal concentration of 10^{-5} mol/L) began at a pH of 6 for copper.[22] In addition, it can be seen from Figure 2 that at pH 2.0 about 24.1% Cu^{2+} ions can be adsorbed on SCAM-1. The experimental results indicate that as the solution pH increases, the onset of adsorption occurs before the beginning of hydrolysis for the Cu^{2+} ions. Moreover, it is further proved that the solution pH plays an important role in the adsorption process.

Effect of Concentration

The adsorption experiments were conducted in a series of Cu^{2+} solutions with different initial con-

centrations. The percentage of removal of Cu^{2+} ions by SCAM-1 decreased from 100 to 29.8% (Fig. 3) when increasing the initial concentration of Cu^{2+} ions from 31.8 to 381.0 mg/L at pH 5.0 and 10°C. It can be noted from the figure that the adsorption of Cu^{2+} ions on SCAM-1 is highly concentration dependent.

Adsorption Isotherms

The adsorption isotherm for the adsorbed Cu^{2+} ions on SCAM-1 can be analyzed by both the Freundlich and Langmuir isotherms.

The linear representation of the Freundlich adsorption equation is expressed as[23]

$$\log qe = \log k + \frac{1}{n} \log C_e \qquad (5)$$

where $qe = (C_0 - C_e)/W$; C_0 and C_e are the initial and equilibrium concentrations of the Cu^{2+} ions in solution, respectively (mg/L); qe is the milligrams of adsorbed Cu^{2+} per gram of adsorbent (mg/g); W is the amount of adsorbent required to adsorb Cu^{2+} ions (g); and k and $1/n$ are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the capacity and intensity of adsorption, respectively.

The adsorption of Cu^{2+} ions on SCAM-1 was found to correspond with the Freundlich adsorption isotherm (Fig. 4). The Freundlich adsorption equation is as follows:

$$\log qe = 1.4094 + 0.2672 \log C_e \qquad (6)$$

where $k = 25.67$ and $1/n = 0.2672$. The results show that the adsorbent has a high adsorption capacity, and the adsorption of Cu^{2+} ions on SCAM-1 is feasible ($1/n = 0.2672$).
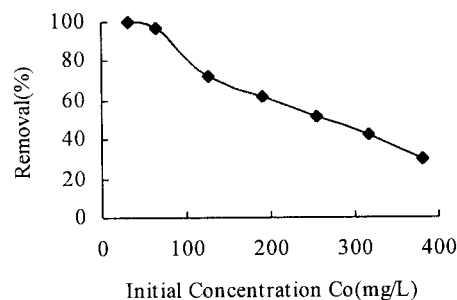

Figure 3 The effect of the initial concentration on the adsorption efficiency at pH 5.0 and 10°C for 120 min.
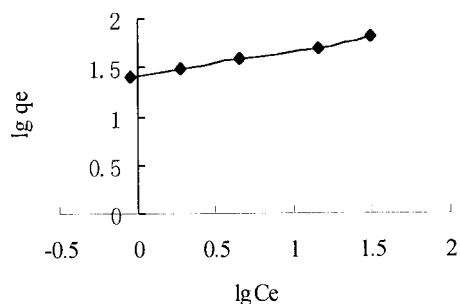
Figure 4 A Freundlich plot for the adsorption of Cu^{2+} on SCAM-1 at pH 5.0 and 10°C with 63.5 mg/L Cu^{2+}.

The linear representation of the Langmuir isotherm can be expressed as

$$\frac{C_e}{qe} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (7)$$

where Q_0 is the maximum amount of adsorbed Cu^{2+} per gram of adsorbent (mg/g) and b is the Langmuir constant (L/mg). Thus, a plot of C_e/qe versus C_e should yield a straight line having a slope $1/Q_0$ and an intercept of $1/Q_0b$ from which the values of Q_0 and b may be readily obtained.

The plot of C_e/qe versus C_e gave a straight line (Fig. 5). Figure 5 shows that the adsorption behavior follows the Langmuir adsorption isotherm. The Langmuir isothermal adsorption equation is as follows:

$$\frac{C_e}{qe} = 0.03339 + 0.01555C_e \qquad (8)$$

where $1/Q_0b = 0.03339$ and $1/Q_0 = 0.01555$. Hence, the values of Q_0 and b are 64.31 mg/g and 0.4656 L/mg, respectively.

The validity of the Langmuir isotherm was further confirmed by regression analysis of the data at 10°C. The regression relating C_e/qe and C_e at 10°C is found as

$$\frac{C_e}{qe} = 0.03337 + 0.01556C_e \qquad (9)$$

By comparing eqs. (7) and (9), the values of Q_0 and b are 64.29 mg/g and 0.4661 L/mg, respectively, which are in good agreement with the graphical values at 10°C.

The favorable nature of adsorption can be expressed in terms of a dimensionless separation factor of a equilibrium parameter, which is defined by[24,25]

$$R_L = \frac{1}{(1 + bC_0)} \qquad (10)$$

The R_L value for Cu^{2+} ion uptake is 0.03272, which is less than 0.1, indicating favorable adsorption.

Effect of Temperature

The adsorption behaviors of adsorbed Cu^{2+} ions on SCAM-1 at 10, 20, 30, and 40°C also follow the Langmuir adsorption isotherm. The Q_0 of SCAM-1 for the uptake of Cu(II) increases from 64.31 to 83.56 mg/g by increasing the temperature from 10 to 40°C, indicating the process to be endothermic (Table II). The increase in uptake of Cu^{2+} ions with temperature may be due to the enhanced rate of intraparticle diffusion of adsorbate and changes in the size of the pores.

The change in the apparent enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) of adsorption were calculated using the following equations:

$$\ln b = \ln b' - \frac{\Delta H}{RT} \qquad (11)$$

$$\ln b = -\frac{\Delta G}{RT} \qquad (12)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (13)$$

The ΔH of adsorption, as determined from the slope of $\ln b$ versus $1/T$, is equal to 23.99 kJ/mol, which suggests the possibility of strong bonding between the adsorbate and adsorbent. The results
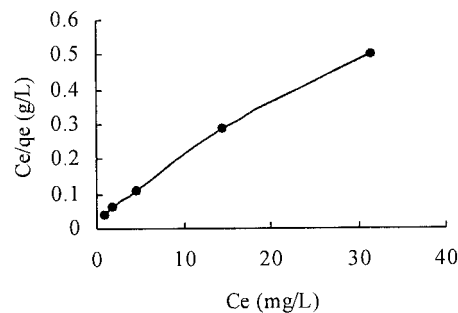

Figure 5 A Langmuir plot for the adsorption of Cu^{2+} on SCAM-1 at pH 5.0 and 10°C with 63.5 mg/L Cu^{2+}.

Table II   Langmuir Constants and Thermodynamics Parameters at Different Temperatures

Temp. (°C)	Langmuir Constant		Thermodynamic		Parameters
	Q_0 (mg/g)	b (L/mg)	$-\Delta G$ (kJ/mol)	ΔS (J/mol)	ΔH (10–40°C) (kJ/mol)
10	64.31	0.4656	24.23	170.30	
20	70.52	0.6591	25.94	170.32	23.99
30	77.02	0.9120	27.69	170.47	
40	83.56	1.235	29.34	170.30	

indicate that the adsorption process is endothermic and temperature dependent. The values of ΔG are negative and decrease with increasing temperature, demonstrating an increase in the feasibility of adsorption at higher temperatures.[26] The positive value of ΔS suggests some structural changes in the adsorbate and adsorbent.

Effect of Salts

Sometimes dissolved salts, like NaCl, Na_2SO_4, $MgCl_2$, $CaCl_2$, and so forth, may also be present in the wastewaters containing Cu^{2+} ions. Moreover, the presence of these salts may affect the adsorption treatment of Cu^{2+} ions. Therefore, the adsorption of Cu^{2+} ions on SCAM-1 was studied in the presence of various concentrations (0–1.0 mol/L) of inorganic salts such as NaCl, Na_2SO_4, $MgCl_2$, and $CaCl_2$ at 10°C. Because the concentration of NaCl or Na_2SO_4 is below 0.5 mol/L, there is no effect on the adsorption of Cu^{2+} ions on SCAM-1. Also, even higher concentrations of NaCl or Na_2SO_4 do not cause any significant effect (<3.6%). In the concentration range of 0–1.0 mol/L, the presence of $MgCl_2$ and $CaCl_2$ do not affect the adsorption of Cu^{2+} ions significantly (<5.1%). The above results suggest that the adsorption of Cu^{2+} ions on SCAM-1 is evidently almost unaffected by the presence of such inorganic salts as NaCl, Na_2SO_4, $MgCl_2$, and $CaCl_2$.

Desorption Tests

In order to repeatedly use the adsorbent and to recover the Cu^{2+} ions, the adsorption tests were conducted with various concentrations of HCl or NaOH aqueous solutions. The results are summarized in Table III. Table III shows that the recovery percentage is 62.1–100% using a HCl or NaOH solution. The results indicate that the ad-

sorbed Cu^{2+} ions SCAM-1 can be recovered by treating it with a HCl or NaOH solution, and a greater recovery rate can be obtained when a HCl solution is used. Moreover, almost 100% of the Cu^{2+} ions can be recovered when a 2.0 mol/L HCl solution is used.

Readsorption Tests

Readsorption tests were also carried out to evaluate the practical utility of SCAM-1. After 10 replications of adsorption and desorption, almost no loss of adsorption capacity is observed. Only 2.6% of the adsorption capacity decreases after 20 cycles. After 30 cycles the lost adsorption capacity reaches 7.2% (Fig. 6). The results indicate that SCAM-1 is a promising adsorbent in the treatment of copper-bearing wastewaters.

Comparison Tests

The adsorption and desorption tests were conducted by comparing SCAM-1 with a weakly acidic cation exchange resin (R724) containing partially dissociated carboxyl active groups under otherwise identical conditions. The adsorption capacities of SCAM-1 and R724 are 30.8 and 26.6

Table III   Recovery Rate of Adsorbed Cu^{2+} Ions on Adsorbent

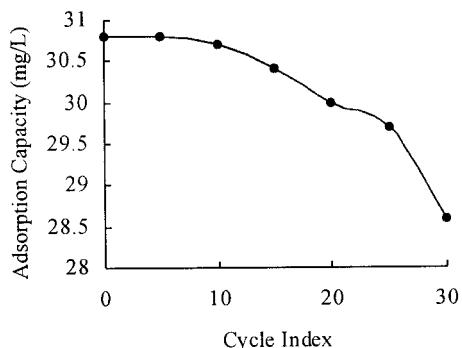| Solution	Concnt (mol/L)	Recovery Rate (%)
HCl	0.5	71.6
HCl	1.0	98.7
HCl	2.0	100
NaOH	0.5	62.1
NaOH	1.0	93.6
NaOH	2.0	98.9

Figure 6 Adsorption–desorption cycles of Cu^{2+} ions on SCAM-1. The adsorption conditions are pH 5.0 and 10°C for 120 min with 63.5 mg/L Cu^{2+}; the desorption conditions are 10 mL of HCl (2.0 mol/L) for 120 min.

mg/g, respectively. The adsorption capacities of both the adsorbents are decreased by increasing the initial concentration of Cu^{2+} ions at pH 5.0 and 10°C. The adsorption capacity of SCAM-1 is a little higher than that of R724, indicating the adsorption of Cu^{2+} ions on SCAM-1 may be related to the chemical and physical properties of SCAM-1 (Table I).

The recovery percentages of adsorbed Cu^{2+} ions on SCAM-1 and R724 are 100 and 87.2%, respectively, when a 2.0 mol/L HCl solution is used. Also, the adsorption of Cu^{2+} ions on R724 is significantly affected by the presence of inorganic salts such as NaCl, Na_2SO_4, $MgCl_2$, and $CaCl_2$. The adsorption capacities of SCAM-1 and R724 decrease to 30.7 and 19.2 mg/g, respectively, when the concentration of $MgCl_2$ reaches 0.5 mol/L. The above results further prove that SCAM-1 is a prospective adsorbent in the removal of copper-bearing wastewaters.

CONCLUSION

A new spherical cellulose adsorbent containing the carboxyl anionic group can be used to adsorb and recover copper(II) from aqueous solutions. The adsorption process is dependent on the initial time, pH, concentration, and temperature and follows both the Freundlich and Langmuir isothermal adsorptions. Moreover, a higher temperature favors the adsorption, indicating that the process is endothermic (ΔH = 23.99 kJ/mol). Inorganic salts of NaCl, Na_2SO_4, $MgCl_2$, and $CaCl_2$ show no apparent effect on the adsorption of Cu^{2+} ions. The Cu^{2+} ions adsorbed on SCAM-1 can be recov-ered by treating them with a HCl or NaOH solution. The recovery percentage can reach 100% when a 2.0 mol/L HCl aqueous solution is used. In addition, after 30 replications of adsorption and desorption, only 7.2% of the adsorption capacity is lost.

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