Adsorption of Cu(II) Ions from an Aqueous Solution by Crosslinked Amphoteric Starch

Shi-Mei Xu, Shun Feng, Fan Yue, Ji-De Wang

College of Chemistry and Chemical Engineering, Xinjing University, Urumqi, 830046, People's Republic of China

ABSTRACT: The adsorption process of Cu(II) ions from aqueous solutions by crosslinked amphoteric starch with quaternary ammonium and carboxymethyl groups was investigated. The adsorption capacity was found to be dependent on the solution pH, the dose of the crosslinked amphoteric starch, and the initial concentration of Cu(II) ions. Moreover, the adsorption capacity increased with an increasing degree of substitution (DS) of the carboxymethyl groups. The adsorption followed a Freundlich adsorption isotherm. The adsorption process was endothermic, and the thermodynamic parameters were calculated at different DS values. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 728–732, 2004

Key words: adsorption; modification; thermodynamics

INTRODUCTION

The removal of heavy-metal ions from sewage and industrial wastewater has been given much more attention over the past few years. Among existing methods, reactive polymers have been proved effective.[1–5] Starch is renewable and biodegradable, and modified starch is capable of adsorbing heavy-metal ions; therefore, the use of low-cost modified starch, such as cationic or anionic starch, for the removal of heavy-metal ions has been documented.[6–9] In comparison, amphoteric starch is used in a wider range of applications because it can simultaneously remove metal cations and anions from aqueous solutions. Chan and a coworker[10,11] reported the mass-transport process for the adsorption of Cu^{2+} and Ga^{2+} onto insoluble amphoteric starch containing quaternary ammonium cations and phosphate anions. However, they did not state the relationship between the adsorption capacity and the degree of substitution (DS) of the modified starch, which is very important in actual applications, and the adsorption behavior of Cu(II) ions and amphoteric starch with carboxymethyl anionic groups of different DS values has not been reported so far in the relevant literature.

Recently, the adsorption process of metal anions by amphoteric starch with quaternary ammonium and carboxymethyl groups was investigated by our laboratory.[12] This study concerned the removal of Cu(II) ions from aqueous solutions by crosslinked amphoteric starch (CAS) and examined the effects of the initial pH, the dose, and the initial concentration. The adsorption isotherm and thermodynamic parameters were also calculated.

EXPERIMENTAL

Materials

Corn starch (food-grade) was dried at 105°C before it was used. 3-Chloro-2-hydroxypropyltrimethylammonium chloride (a 65% aqueous solution), epichlorohydrin, and chloroacetic acid (an analytical reagent) were used as received. An atomic adsorption spectrophotometer (AA 300) from PerkinElmer Co. (Singapore) was used.
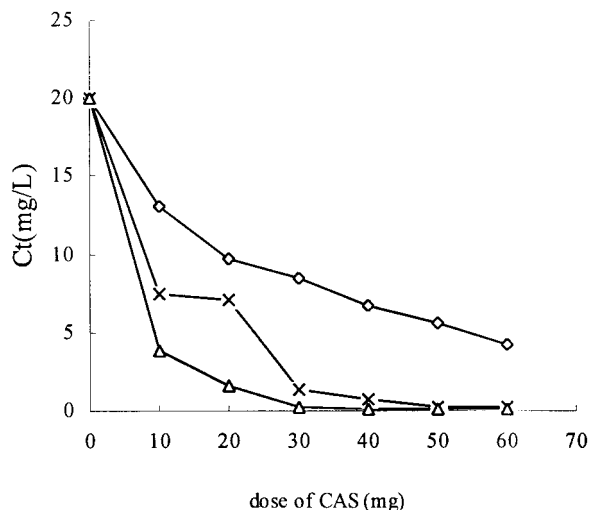
CAS was prepared by a semidry process according to a previous work.[12] The nitrogen content and DS value of the quaternary ammonium cationic groups in CAS were measured with the Kjeldahl method; the amount and DS of the carboxymethyl anionic groups was measured according to Eyler and Diephuis's work.[13] Three types of CAS were used in these experiments, and they were named CAS1, CAS2, and CAS3. The DS value of the quaternary ammonium cationic groups was 0.3 for all of them, whereas the DS values of the carboxymethyl anionic groups were different: 0.12, 0.20, and 0.33, respectively.

Adsorption procedure

The adsorption experiments were carried out in a series of 100-mL Erlenmeyer flasks containing the desired dose of CAS and 50 mL of an aqueous $CuCl_2$ solution at the desired concentration and initial pH (adjusted with 0.1N hydrochloric acid or 0.1N NaOH) in a shaking bath. After a certain period of shaking, the supernatants were removed, and the concentration

of Cu(II) after the adsorption was analyzed with an atomic adsorption spectrophotometer.

The adsorption capacity of CAS (Q; mg/g) was calculated as follows:

$$Q = \frac{(C_0 - C_t)V}{m}$$

where C_0 and C_t are the concentrations of Cu(II) ions in the beginning and at time t, respectively (mg/L); V is the total volume of the aqueous solution (L); and m is the weight of CAS (g).

The aforementioned reaction process can be described as follows:

RESULTS AND DISCUSSION

Effect of the pH

Metal-ion adsorption is known to be dependent on the pH of a solution (see Fig. 1). The residual concentration of Cu(II) ions decreases significantly as the pH increases from 2 to 8, but it increases abruptly when the pH is 10. At the same pH value, as the level of anionic groups increases, the adsorption capacity of the adsorbent increases (i.e., $Q_{CAS1} < Q_{CAS2} < Q_{CAS3}$).

At low pH values, carboxymethyl groups exist in the form of —COOH, and they prevent the adsorption of Cu(II) ions onto CAS. The chelation between CAS and Cu(II) ions is stronger at higher pH values, as shown in Figure 1. Moreover, the carboxymethyl groups in CAS are responsible for the interaction; the adsorption is more effective when the DS of the carboxymethyl groups is higher.

When pH is greater than 8, the residual concentration of Cu(II) ions increases abruptly; perhaps because Cu(II) ions are precipitated in the form of $Cu(OH)_2$, under alkaline conditions, flocculation is dominant. To avoid precipitation, we carried out the following experiments at pH 6, at which higher adsorption was achieved.

Effect of the dose

The residual concentrations of Cu(II) ions for absorbent doses ranging from 10 to 60 mg at 20 mg/L Cu(II) ion and 20°C are shown in Figure 2.

The residual concentration of Cu(II) ions decreases with an increasing dose of CAS and reaches 6.7, 0.78, and 0.15 mg/L, respectively, even with a 40-mg dose. Furthermore, the DS of carboxymethyl groups in CAS leads to the difference in Q. Moreover, as far as im-

Figure 1 Effect of the initial pH value of a solution on the residual concentration of Cu(II) ions: (◇) CAS1, (×) CAS2, and (△) CAS3 ([Cu^{2+}] = 20 mg/L; t = 1 h; T = 20°C; CAS dose = 30 mg).
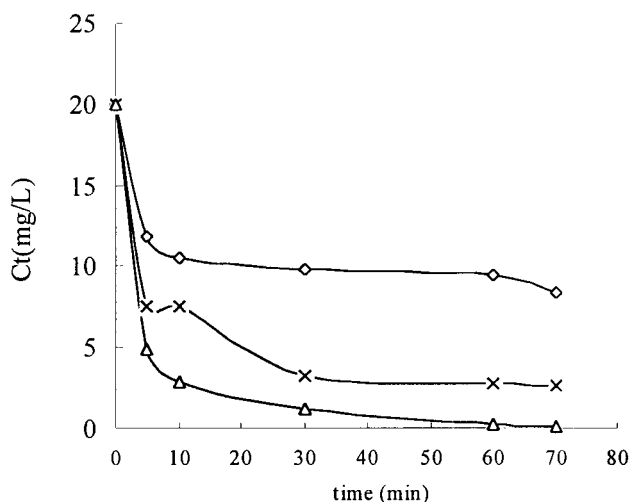
Figure 2 Effect of the dose on the residual concentration of Cu(II) ions: ($\diamond$) CAS1, ($\times$) CAS2, and ($\triangle$) CAS3 ([Cu^{2+}] = 20 mg/L; t = 1 h; T = 20°C; pH = 6.0).

Figure 4 Effect of the initial concentration of Cu^{2+}: ($\diamond$) CAS1, ($\times$) CAS2, and ($\triangle$) CAS3 (pH = 6.0; t = 1 h; T = 20°C; CAS dose = 30 mg).

proving Q is concerned, increasing the DS of the absorbents is more effective and economical than increasing the dose of the absorbents.

Effect of the adsorption time

The Cu(II) ion adsorption shows a rapid increase with an increasing DS of the carboxymethyl groups in CAS at first and then slows down and reaches an equilibrium value (Fig. 3). The time for reaching the adsorption equilibrium is approximately 1 h for each DS.

It is well known that adsorption consists of three steps: (1) Cu(II) ions from the bulk solution diffuse through a liquid film surrounding the particle surface,
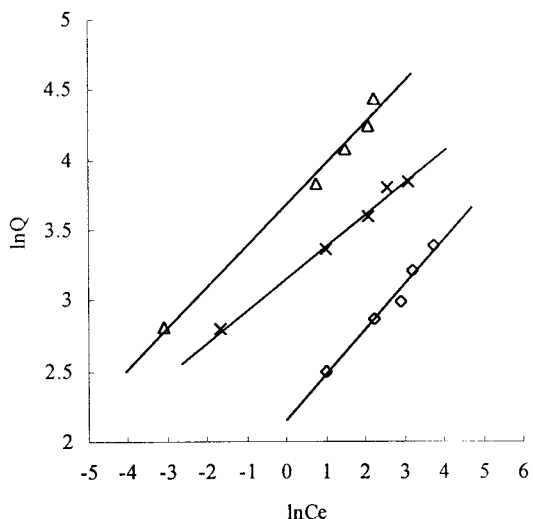
(2) Cu(II) ions diffuse through the particle to the adsorption active site, and (3) Cu(II) ions are adsorbed onto the adsorption active site. The establishment of the rate-limiting step assumes that step 3 is rapid, and so it is not considered in the kinetic analysis. Consequently, steps 1 and 2 are considered rate-limiting steps. The results show that the equilibrium time is almost the same and is independent of the DS of anionic groups. Therefore, it is the particle size that determines the equilibrium rate in steps 1 and 2. The average particle sizes of the absorbents are all 100–120 mesh, so there is no significant difference in the equilibrium time.

Effect of the initial Cu(II) ion concentration

Figure 4 shows the relationship between the Cu(II) ion initial concentration and the residual concentration. The residual concentration of Cu(II) of CAS3, CAS2, and CAS1 increases from less than 0.1 to 9 mg/L, from 0.1 to 25 mg/L, and from 2 to 42 mg/L, respectively, as the initial concentration of Cu(II) increases from 10 to 60 mg/L. Q_{CAS1}, Q_{CAS2}, and Q_{CAS3} are 29.6, 57.8, and 84.4 mg/g, respectively. The three curves of the residual concentrations of Cu(II) versus the initial concentration of Cu(II) are all concave and upward. Moreover, they share a common trend; this implies that the type of adsorption isotherm for the three adsorbents would be the same, being independent of the DS of the anionic groups.

Adsorption isotherms

The Freundlich adsorption isotherm can be expressed as follows:

Figure 3 Effect of the adsorption time on the residual concentration of Cu(II) ions: ($\diamond$) CAS1, ($\times$) CAS2, and ($\triangle$) CAS3 ([Cu^{2+}] = 20 mg/L; pH = 6.0; T = 20°C; CAS dose = 30 mg).

Figure 5 Freundlich adsorption isotherm for ($\diamond$) CAS1, ($\times$) CAS2, and ($\triangle$) CAS3 (pH = 6.0; t = 1 h; T = 20°C; CAS dose = 30 mg).

$$\ln Q = n\ln C_e + \ln K$$

where C_e is the equilibrium concentration of the metal ion in solution (mg/L) and K and n are the Freundlich constants. Freundlich plots of the data of Cu(II) ions adsorbed onto the absorbents are shown in Figure 5, and the adsorption parameters for CAS1, CAS2, and CAS3 are listed in Table I.

The relationship between ln Q and ln C_e is linear, and this indicates that the adsorption behavior follows the Freundlich adsorption isotherm. The results show that CAS3 has a larger adsorption capacity than CAS2, and CAS2 has a larger adsorption capacity than CAS1; that is, a higher DS value of the anionic group leads to a higher adsorption capacity. The same conclusion can be drawn from the Freundlich constant K, used as a measure of the capacity of adsorption: when the DS of the anionic groups increases, K increases from 8.68 to 39.53.
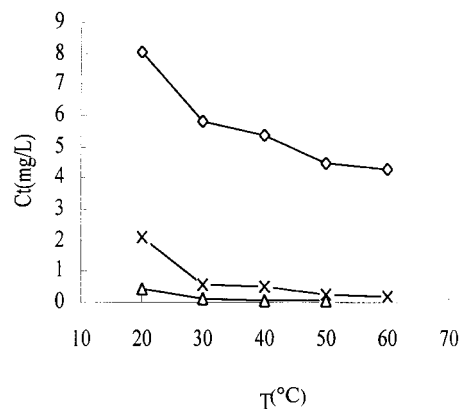
Adsorption thermodynamics

The adsorption behaviors of Cu(II) ions adsorbed onto the adsorbents at different temperatures, ranging from 20 to 60°C, were also investigated (see Fig. 6). The

TABLE I
Freundlich Parameters for CAS1, CAS2, and CAS3 at 20°C

Sample	K	n	r^a
CAS1	8.68	0.32	0.9873
CAS2	23.46	0.22	0.9959
CAS3	39.53	0.29	0.9938

[a] The related coefficient.

Figure 6 Effect of the temperature: ($\diamond$) CAS1, ($\times$) CAS2, and ($\triangle$) CAS3 ([Cu^{2+}] = 20 mg/L; pH = 6.0; t = 1 h; CAS dose = 30 mg).

results show that the adsorption capacity at 20°C is lower than that at 60°C, and this implies that the adsorption process is endothermic. To verify this conclusion, we have plotted $\log(Q/C_e)$ versus $1/T$ for CAS1, CAS2, and CAS3 in Figure 7. Because the relationship between $\log(Q/C_e)$ and $1/T$ for CAS1, CAS2, and CAS3 is linear, the changes in the apparent enthalpy (ΔH^θ) and entropy (ΔS^θ) can be calculated with the Van't Hoff equation:

$$\log\left(\frac{Q}{C_e}\right) = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R}$$

where R is a constant (8.314 J/(k mol)) and T is absolute temperature.

The changes in the free energy (ΔG^θ) can be calculated with the following thermodynamic equation: $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$. The values of ΔH^θ, ΔS^θ, and ΔG^θ
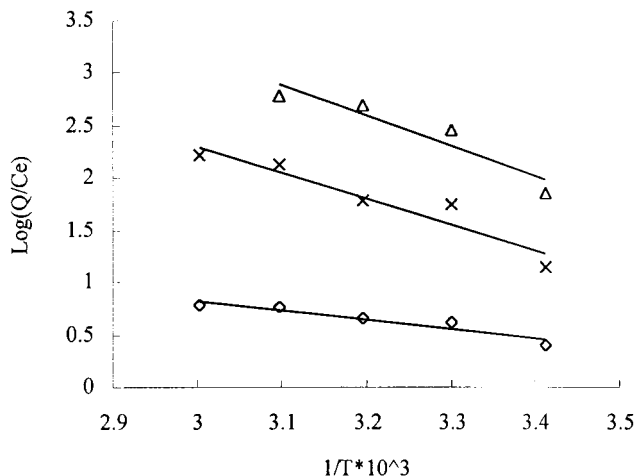
Figure 7 Log(Q/C_e) versus $1/T \times 10^3$ for ($\diamond$) CAS1, ($\times$) CAS2, and ($\triangle$) CAS3 ([Cu^{2+}] = 20 mg/L; pH = 6.0; t = 1 h; CAS dose = 30 mg).

TABLE II
Thermodynamic Values at Various Temperatures for CAS1, CAS2, and CAS3

Sample	Temperature (°C)	Q (mg/g)	ΔG^{θ} (kJ/mol)	ΔH^{θ} (kJ/mol)	ΔS^{θ} (J/mol K)
CAS1	20	19.95	−2.51	17.72	29.98
	30	23.69	−3.20		
	40	24.39	−3.89		
	50	25.89	−4.58		
	60	26.23	−5.27		
CAS2	20	29.85	−7.20	47.35	80.84
	30	32.37	−9.06		
	40	32.44	−10.92		
	50	32.93	−12.78		
	60	33.00	−14.65		
CAS3	20	32.58	−11.10	55.55	98.77
	30	33.14	−13.37		
	40	33.22	−15.65		
	50	33.24	−17.92		

are listed in Table II. The results show that as the temperature increases, Q increases. The adsorption process is endothermic because of the positive value of ΔH^{θ}. In addition, a negative value of ΔG^{θ} demonstrates that it is easy for the adsorption of Cu(II) ions to proceed.

CONCLUSIONS

CAS with quaternary ammonium and carboxymethyl groups can be used to remove Cu(II) ions from aqueous solutions effectively. The adsorption capacity of CAS increases as the DS of carboxymethyl groups increases, and it is dependent on the pH, the dose of the absorbents, and the initial concentration of Cu(II) ions. The time to reach the adsorption equilibrium is independent of the DS of the anionic groups. The adsorption process follows the Freundlich adsorption isotherm, and a higher temperature facilitates the adsorption.

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